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EXTRACT FROM PREFACE TO FIRST EDITION

IN accepting the invitation of the publishers to write a book of a popular character on modern chemical discovery, I am conscious of undertaking a very serious task. The difficulties to be encountered are twofold; first, there is the complexity and diversity of the subjects to be dealt with, and, secondly, the difficulty of rendering an account of many of them in language at once intelligible to the non-technical reader and free from serious inaccuracy. The author is indebted for assistance from many friends, and in connection especially with the chapters dealing with manufacturing processes such help was indispensable.

I am under a special obligation to the Council of the Society of Chemical Industry for permission to adorn the cover of the book with the beautiful obverse of the medal awarded by the Society every two years for discoveries or inventions or other distinguished services rendered to industrial chemistry. The medal was designed by Miss Margaret May Giles (Mrs. Bernard Jenkin). It represents symbolically the four elements of Democritus and Aristotle, namely Earth, Water, Fire, and Air, together with the seven planets, of which the names and symbols were, by the alchemists, associated with the seven metals known in ancient times. The crescent represents Luna, the moon (silver), and in order from left to right follow Jupiter (tin), Saturn (lead), Mars (iron), Mercury (mercury or quicksilver), Venus (copper). The tortoise above and the fish below belong to earth and water respectively. Sol, the sun (gold), occupies the centre.

W. A. T.

PREFACE TO THE SIXTH (REVISED) EDITION

IN revising the late Sir William Tilden's well-known book the writer has attempted to carry out the work in such a way as to bring the subject matter up to date without altering the style and characteristic view-point of the original author. The new material incorporated has been selected so as to fit in with the structure and continuity of the earlier editions : the aim has been to include what Professor Tilden would probably have chosen had he been alive to-day. The additional subject matter is mainly concerned with chemical works laboratories ; theories of atomic structure and of the union of atoms (valency) ; transmutation and disintegration of elements ; artificial radioactivity ; the discovery and significance of " heavy hydrogen " (deuterium) ; the coal and petroleum industries ; synthetic rubber and rubber substitutes ; artificial plastics ; the fixation of nitrogen ; vitamins ; hormones ; and the colouring matters of plants. About fifty new photographs and a number of biographical notices have been included.

This book was originally intended for " non-technical readers " and, as the fifth edition was issued within ten years of the original date of publication, there is little doubt that it was appreciated by such readers. A glance at its pages will show that in addition there are many points which would appeal more especially to those who have some knowledge of science : it is a matter for congratulation that as a result of the general widening of the basis of modern education and of the work of the British Broadcasting Corporation such persons are by no means as uncommon as they were when this book was first written. It is hoped, therefore, that the new edition will have a wide appeal,

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particularly as it is in many ways complementary to the present writer's *Chemistry in Daily Life*.

In carrying out the work of revision the "leaders," articles and reprints of lectures appearing in *Chemistry and Industry* have proved invaluable, and this opportunity must be taken to express indebtedness to that journal and its editor. Thanks are also due to the following individuals and firms for supplying information or for loaning photographs, with permission to publish them: Professor G. T. Morgan, F.R.S.; Dr. R. H. Pickard, F.R.S.; Mr. Philip Tilden, F.R.I.B.A.; Anglo-Iranian Oil Co. Ltd.; Boots Pure Drug Co. Ltd.; British Commercial Gas Association; British Oxygen Co. Ltd.; Chemical Engineering and Wilton's Patent Furnace Co. Ltd.; Falk, Stadelmann and Co. Ltd.; Imperial Chemical Industries Ltd., and its subsidiaries, British Dyestuffs Corporation Ltd. and Lighting Trades Ltd.; Kennicott Water Softener Co. Ltd.; and the Woodhall-Duckham Co. Ltd. The photographs of the Chemical Research Laboratory, Teddington, are Crown Copyright, and are reproduced by permission of H.M. Stationery Office.

In conclusion the writer wishes to express his sincere thanks to his wife for help in collecting the material for the new edition, in the revision of the manuscript and in correcting proofs.

S. G.

SHEFFIELD,

September, 1935.

CHEMICAL DISCOVERY AND INVENTION IN THE TWENTIETH CENTURY

CHAPTER I

INTRODUCTION

IN selecting the subjects to be dealt with in the following pages the writer has been influenced by the reflection that the nature of the operations in which the chemist is engaged, the objects he has in view, the subjects and methods of study, and the uses to which his theories may be applied are still very little understood by the public. It is therefore to be hoped that readers may be assisted in forming new views about all these subjects, and any confusion existing in their minds concerning them may be cleared away. Considerable enlightenment may be hoped for from the fact that in nearly all the universities in the world at least one professor of chemistry is now to be found, while in most of the modern universities it is recognised that the subject extends over too wide a field to be efficiently cultivated by one man, and three main divisions are generally recognised, namely, inorganic, organic, and physical chemistry. To these are sometimes added departments of applied chemistry in which the relations of systematic chemistry to industry or manufacture, such as fuel, metallurgy, dyeing, and bleaching, etc., are studied. But the extension of knowledge from the universities to the mass of the people is still a slow process, and notwithstanding the quickening effect which recent events have produced on the public mind in England at any rate, it will be long before the practical economic importance of a knowledge of chemistry will be fully recognised by Government departments, municipalities, and the public generally.

The ignorance of scientific things which exists among people commonly said to be well educated can only be regarded as scandalous, but evidence as to the gullibility of the public is supplied daily by every newspaper. To confuse Faraday with Fahrenheit may be thought a fallacy which offends only against sentiment, but the grossest practical mistakes would be avoided if a small amount of knowledge of principles and some capacity for independent observation were in the possession of everyone.

In the Sixth Norman Lockyer Lecture, delivered before the British Science Guild on November 13th, 1930, Sir William Pope, Professor of Chemistry in the University of Cambridge, said : " Some time since I was asked by a group of City men to inspect and report on a commercial process for converting one of the common metals into another of about ten times the value ; it appeared they had already spent money on testing the practicability of the process. I replied that it was unnecessary for me to inspect the process, as I could report at once that it was a fraud. My friends were, however, so convinced of the *bona-fides* of the process, by experiments which they had seen, and by analyses made by reputable assayers, that I went to see the operation in the hope that I might prevent them from wasting more money. The inventor of the process told me he knew no chemistry, and then poured out a flow of alchemistic jargon . . . the fakir then melted up a quantity of base metal, of which he gave me a sample, and stirred a small pellet of the ' seed ' into the molten mass ; after some period of solemn contemplation, he announced that the heating must now be continued for eight hours. . . . As I could not stay . . . and . . . could not know what substitution might be effected during my absence . . . I stated the conditions of a test which would satisfy me. . . . These conditions were willingly accepted and the necromancer assured me that the necessary materials would be in my hands within a couple of days ; as I knew would be the case, nothing was forthcoming, and the whole project fell through.

" This incident may seem so ridiculous as to be hardly worth describing . . . ; I have gathered, however, that some scheme or other for converting base metals into more valuable ones is practically always under consideration by one or other City group of financiers. . . . Needless to say, such fantastic schemes would never occupy the attention of anyone who had received the broad, scientific education for which I am pleading."

With regard to the branch of Science called Chemistry and to its applications one considerable source of confusion in England is to be found in the fact that the name *Chemist* has long been associated with the calling which is more appropriately styled "pharmacy," that is the dealing with drugs (*φάρμακον*, a medicine or drug).

In Germany the compounder of medicines is entitled "apotheker," while in France he is called a "pharmacien." In the British Isles, however, the assumption of the title Chemist and Druggist for a century or more by the competitors of the apothecaries has become so completely established in the public mind that to speak of a chemist invariably implies in common parlance the person who compounds and sells medicines. And this custom has been ratified by the Act of Parliament (Pharmacy Act, 1868) which secures to the members of the pharmaceutical body the exclusive right to the title "Chemist and Druggist" or "Pharmaceutical Chemist," according to their qualifications. It is not to be denied that a small number of pharmacists do actually possess such a knowledge of chemistry as to qualify them to undertake analytical work or to manufacture chemicals or pursue chemical research, but this is not the essential part of their calling, and the anomaly lies in the fact that if Sir Humphry Davy himself were now living he could not legally call himself a chemist, his name not being on the pharmaceutical register.

Chemistry has for centuries been associated, perhaps naturally, with medicine, and, confining attention to modern times, it is easy to recall the names of many men who became eminent as chemists having begun by the study of medicine in some form or other. Black, Davy, Berzelius, Wollaston, Wöhler, Wurtz, Andrews, and W. A. Miller began by the study of medicine, while Scheele, Rose, Liebig, Dumas, and Frankland received their earliest notions of chemistry in the druggist's shop.¹

Chemistry has been gradually emancipated from these associations with enormous advantages to the progress of knowledge. The systematic study of chemistry and provision for teaching it in schools and universities belong to comparatively recent times.

In the middle of last century there were no laboratories for

¹ It may be of interest to note here that Sir William Tilden was himself first introduced to chemistry through pharmacy.

practical work in any of the British universities and chemistry was not a subject which led up to a degree. The Professor of Chemistry at Oxford was also Professor of Botany, while at Cambridge the Professor of Chemistry was a country clergyman who came up once a year to give a course of lectures, and it was even thought very creditable on his part to do so much. In those days no school had a resident science master who gave the whole of his time to teaching elementary physics or chemistry, though a few received a visit about once in a fortnight from a peripatetic teacher who brought with him a box containing portable apparatus.

Happily times are changed in all these respects and, notwithstanding the substantial grounds for hoping that still greater progress will be made, the position of the science master in all the most important schools is now fully assured. But the conflict between literature and science for the possession of endowments, time of teachers and pupils, energy of both, and prominence in the educational field is even now not at an end, and never will cease until both sides are duly influenced by respect for the work and aspirations of the other.

From the circumstances connected with the great war in Europe the importance of a knowledge of chemistry has become particularly prominent. The appropriation of the larger part of the manufacture of dyes and drugs by Germany has attracted particular attention, especially in those countries in which such industries have been less developed, and it has become at last obvious to the public that the imperfect recognition of the value of scientific knowledge is the main cause of their deficiencies. That this has been known to chemists during the last forty years is made evident by the numerous speeches, papers, and presidential addresses which have been issued by some of the most eminent professors of chemistry in the United Kingdom.

Fortunately, since the war the position with regard to research has been considerably improved. Not only did the Government subsidise the dyestuffs industry in Great Britain to the extent of over a million pounds sterling, so that it is now effectively self-supporting, but in addition steps were taken in 1915 which resulted in the formation on December 15th, 1916, of a Department of Scientific and Industrial Research operating under the guidance of an Advisory Council consisting of a number of eminent scientists and industrialists. This Department has

operated successfully since its inception, and, besides other functions referred to later, it has been instrumental in the formation of some twenty Research Associations, by means of which firms not themselves able to support research laboratories capable of undertaking the larger problems of an industry can combine with others having similar interests. To quote from the recent reports of the Department of Scientific and Industrial Research¹ "... a research association is an organisation, established under the Companies Act, for co-operation in research by firms in an industry or a group of related industries, limited by guarantee and trading without profit in the form of dividends. . . . The essential character of these bodies is that they enjoy full responsibility for the discharge of their functions. They appoint their own staff, make their own arrangements for carrying out research work, and draw up their own programmes," that is to say without interference from the Government Department. "They also settle how the results of the research are to be made available to members, though the Department retains a right of veto over the communication of results abroad." In addition to studying the future possibilities of the industry the laboratories of the research associations pay attention to day-to-day problems as well as to the individual problems of constituent firms.

Grants have been made to research associations by the Department of Scientific and Industrial Research from a sum of one million pounds voted by Parliament in 1917, and although this fund was virtually exhausted in 1934 provision has been made for annual votes to the Department. The expenditure of this money has attracted about one and three-quarter millions sterling from industry, and in recent years the Department has contributed between £60,000 and £70,000 annually towards the cost of research associations, whereas the industries concerned have expended between two and three times these sums. It is the policy of the Department that each association should ultimately become a self-supporting organisation, maintained by industry. The extent of the achievement of the past eighteen years will be realised from the titles of the chief research associations now in existence; they are the Cast Iron; Iron and Steel Industries, Non-Ferrous Metals; Refractories; Electrical and Allied Industries; Scientific Instrument; Paint, Colour, and Varnish; Automobile Engineering; Cotton Industry; Wool

¹ These are published annually by H.M. Stationery Office, price 9d.

Industry; Linen Industry; Silk; Launderers'; Leather Manufacturers; Boot, Shoe, and Allied Trades; Rubber Manufacturers; Flour Millers; Cocoa, Chocolate, Sugar Confectionery, and Jam; Food Manufacturers; and Printing. The net annual output of the industries involved, after deducting the cost of all raw materials, is about £440,000,000, and they provide about one-half of the total exports of Great Britain. The annual expenditure of a "sum of less than a quarter of a million pounds is trivial in relation to the interests involved and the possibilities awaiting realisation. . . . And inadequate resources continue to hamper research associations in all directions." Nevertheless, an important step in the right direction has been taken from which British industry has undoubtedly benefited.

This movement, however valuable as an encouragement to reform, will not afford a permanent guarantee of commercial success unless the spirit of respect for accurate scientific knowledge and its daily application by highly qualified chemists within the works themselves are diffused generally among the manufacturers. It has been alleged that the universities have not provided the sort of instruction required by students who look forward to employment of a technical character, that the subjects taught have been too far removed from possible applications to industrial purposes and that the habits and methods of research have been neglected. So far as research is concerned it may be that in times now long past the British universities have been to blame, but during recent years such allegations can no longer be sustained.

In this connection the Department of Scientific and Industrial Research has also played an important part by the award of monetary grants of different types. On the recommendation of his professor a student of ability, who appears to have the necessary mental and practical capacity, can obtain a maintenance grant for two years, after taking his bachelor's degree, in order to allow him to be trained in research methods. Larger financial grants are also awarded to investigators of experience either to enable them to carry on their own researches or else to allow them to employ skilled assistance in the study of a specific problem. During the year 1933-4 the Department expended a total of £25,850 in these grants to research workers; this is quite an appreciable sum, but it must be remembered that it

was divided between a number of sciences, although chemistry, in view of its importance, obtained a large share.

The chief advantage to be expected from this scheme is, however, probably not to be found merely in the development of research in the universities and colleges. It is rather to be hoped that this recognition of the importance of training a larger number of young men in scientific methods will operate in stimulating public interest in such matters and rousing it out of the state of indifference which has so long prevailed.

And when the relative importance of "pure" chemistry and "applied" chemistry is considered it seems, at least to the writer, that the former stands clearly first. For all history of science shows that progress has been accomplished only when research has been released from the restrictions with which it is trammelled when the eye of the worker is on the look-out only for immediately useful results.

The Atomic Theory of Dalton and later Kekulé's theory of the benzene ring must have appeared to contemporary manufacturers as mere academic theses of no industrial import. But we have it on the testimony of a very eminent colour-maker that the benzene theory lies at the foundation of the industry. In fact where science has been respected and scientific knowledge cultivated there has been industrial success; where it has been neglected industrial failure has been the consequence.

On the other hand, it seems quite practicable to avoid the reproach which has been so often cast by the practical man at the higher chemical schools, by bringing more prominently and more frequently before the student problems which are connected with industry. This can be easily done by the judicious teacher without loss to the academic value of the training given. For a variety of reasons which are obvious the actual investigation of questions connected with industrial processes cannot be undertaken profitably before an advanced stage is reached in the student's career.

Admitting that there is need for closer attention to the use of science for practical ends, it seems scarcely open to doubt that the greatest benefits to the world have accrued from the pursuit of knowledge for its own sake, and without regard to the possible applications of the knowledge gained to immediate useful purposes. Without such untrammelled enquiry the world would be still in the condition of Europe in the Dark Ages. The relation

of the earth to the sun and the rest of the heavenly bodies, the cause of the seasons, the effect of the atmosphere and its several constituents on plant life and the respiration of animals, the composition of common air and water, and the knowledge of the earth's surface facilitated to every traveller by modern means of locomotion would be still unknown. These things are surely of greater political, social, and moral importance to the human race than even the modern valuable discoveries of new dyes, new drugs, or new sources of light. The possession of such knowledge distinguishes the civilised man from the barbarian and the savage, and is the foundation of all the future hopes of mankind so far as life on this earth is concerned.¹

As already mentioned the number of chairs of Chemistry in the universities is gradually increasing, and each one forms a centre from which many chemical students pass into the outside world and so help in the diffusion of knowledge which may, and frequently does, become very valuable in a practical sense. The university laboratories are also at the present day the source of a good deal of positive knowledge derived directly from researches carried on within their walls. It was not always so, and within the last forty years many reproaches have been directed against the British universities on account of the comparatively small part formerly played by these schools in the production of new chemical knowledge. The departure of so large a proportion of the coal tar colour industry, which originated in this country, to Germany, where the connection between the universities and the chemical industries of that country has been more definite and intimate, has been repeatedly attributed to the want of mutual respect between academic learning and industrial needs. This want of co-ordination has doubtless something to do with the neglect of science generally by the British Government. But amid the many evils of the European war one good seems likely to arise and that is the awakening of the authorities and the public to the necessity of scientific principles in the work of the Empire, and the utilisation of the knowledge and skill of trained scientific men. Hitherto a large part of the intellect of the country has been attracted into other callings and the career open before a highly trained university or other student of science has offered little temptation either in emoluments or

¹ See "Modern Scientific Research," a lecture by Sir W. A. Tilden. *Nature*, Vol. LXXXV, Nov. 3rd, 1910.

social position. There is now some considerable ground for hope that this is being changed.

The study of chemistry as a subject of intellectual interest or of commercial importance has led to the formation of various associations of persons engaged in the same pursuit. Formerly a discovery was usually communicated to the world through the medium of one of the Academies of which one generally exists in each of the chief countries of Europe, and is represented in our own country, so far as physical and natural science is concerned, by the Royal Society which was founded in the reign of Charles the Second. The British Academy founded in 1902 is an institution having somewhat similar aims, but is composed of men distinguished in literature, history, and philosophy.

As to chemistry the institutions of greatest importance in Britain are the following. The oldest of these bodies is the Chemical Society of London, founded in 1841. The objects of the Society were then defined to be chiefly—"The promotion of Chemistry and of those branches of Science immediately connected with it by the reading, discussion, and subsequent publication of original communications." This object has been carried into full effect, and the Journal of the Chemical Society is now the recognised repository of most of the purely scientific researches carried out in the British Empire. In conjunction with the Society of Chemical Industry (see below) it publishes abstracts of nearly all papers on theoretical and industrial chemical subjects, amounting to about 40,000 each year, published in foreign journals. The Society numbers upwards of 3,600 Fellows, and occupies apartments provided by the Government in Burlington House.

The Société Chimique de Paris, founded in 1858, the Berlin Chemical Society, founded in 1867, and the American Chemical Society, founded in 1876, are engaged in similar work in their respective countries.

The Society of Chemical Industry (which includes American, Canadian, and Australian sections) has about five thousand members; it was started in 1881, and, as its name implies, has for its object the study and publication of papers relating to the application of chemistry to manufacturing or other practical purposes. The membership of all these societies implies no professional qualification, but some forty years ago a proposal

was brought forward among the Fellows of the Chemical Society to restrict the Fellowship to persons who could produce evidence of scientific training and qualifications for practice as analytical and advising chemists. This after prolonged discussion was found to be impracticable and a new body was formed, namely, the Institute of Chemistry of Great Britain and Ireland, which in 1885 received a Royal Charter. The Institute holds periodical examinations, and in other ways tests the qualifications of candidates for its Associateship and Fellowship. The Institute stands therefore toward the profession of chemistry somewhat in the same relation as the Institutions of Civil and Mechanical Engineers to the calling of Engineers. It does not possess the exclusive powers of the Royal Colleges of Physicians and Surgeons, but the value of the Fellowship is now recognised by many Government Departments.

The passing in 1872 of the first Adulteration Act, designed to check the adulteration of food, led to the formation in 1874 of the Society of Public Analysts, later extended to include others interested in analytical chemistry. The objects of the society, amongst others, are "to study questions relating to the adulteration of articles of food, drugs, and commercial products generally, and means for its detection; and to promote the efficiency and proper administration of the laws relating to the repression of adulteration."

Other voluntary associations of chemists interested in particular applications of chemistry exist, but sufficient has been said to indicate the nature and extent of the organisation now existing in the British Isles.

As it often happens that parents are uncertain how to gratify the aspirations of a boy to become a chemist a few remarks may be made here as to the course most advisable to pursue.¹ It may be added that there is nothing in the nature of things to prevent a woman following the same course of study. A few women students have successfully taken up chemistry, and they now occupy in most cases important positions as teachers. It is advisable at the outset to point out that success can only be looked for by those who have had a sound general education and that the course of study to be pursued after school age extends over at least four years and may in many cases be

¹ See *The Profession of Chemistry*, by R. B. Pilcher, Registrar of the Institute of Chemistry.

usefully prolonged to five or even six years before entry on professional or industrial life.

If the student enters one of the universities with a view to the pursuit of a science course three or four years from matriculation will be occupied according to the quality of the degree which he wishes to take. His studies up to this point will extend into several branches of science, especially mathematics, physics, and chemistry. Having secured his degree he should then devote one or two years to special chemical work or research under the direction of his teachers. Should he not be in a position to enter one of the universities he may attend the courses of instruction given in one or other of the great technical institutions such as the Imperial College of Science and Technology at South Kensington. Students, however, are not admitted to these institutions without giving evidence of good general education, and four years will generally be occupied in securing the diploma. In all such cases it is necessary to bear in mind that a thorough grounding in general principles is essential to the successful study of the technical applications of the different branches of science concerned. Mathematics and physics are becoming more and more indispensable to the student of chemistry.

Reference has been already made to the grants given by the Department of Scientific and Industrial Research to students who wish to be trained in research ; in addition many universities have special scholarships for the same purpose. Other organisations, such as the Salters' Institute of Industrial Chemistry and the Ramsay Memorial Fund, offer Fellowships to enable university graduates to undertake research work in chemistry, but these are only awarded to men and women of outstanding merit who show promise of becoming leaders in their profession.

The question of the supply of materials and apparatus for research work, which are often expensive, is one frequently perturbing the investigator. The Chemical Society has a small research fund from which grants are made for the purchase of chemicals, but as these seldom exceed £10 other sources of assistance must be sought. The Royal Society administers an annual grant of a few thousand pounds from the Government for a similar purpose, but the amount is quite inadequate to the requirements of many applicants from the whole circle of the sciences. In recent years Imperial Chemical Industries Ltd. have

rendered a great service to research workers in pure chemistry by the donation of sums of from £50 to £100 to the chemistry departments of universities for the purchase of research materials or apparatus. There is no necessity for the research to be of an industrial character: the only restriction is that British made products should be purchased if at all possible.

The relation of our educational systems to practical ends in manufactures and in trade and commerce has been the subject of much discussion in recent times. So also has the difficult problem as to the arrangements whereby manufacturers can make use of scientific assistance and the chemists engaged for industrial employment can gain that knowledge of the business into which they are introduced that alone can enable them to apply their scientific training and skill to the problems confronting them in the works.

There can be no doubt that in the universities and colleges, and perhaps also in secondary and even elementary schools, the view to practical applications of knowledge will in future be kept more distinctly before both teachers and taught. Incentives to industry and concentrated attention will probably be found for the majority of both boys and girls when they realise that what they are expected to learn at school will have a direct influence on their material progress when they go out into the world. The relation of man to the universe in which he finds himself will continue to exercise a fascination sufficient for the exceptional few, but it is probable, and doubtless for the best that "bread-and-butter" studies will continue to be most attractive to the many. The most serious charge which can be preferred against the time-honoured classical system of education is not so much that a knowledge of two dead languages and their literature has but little to do with the conditions of modern life, but that in consequence of the defective methods of teaching hitherto prevalent, school teachers have failed to communicate to the great majority of the pupils any real knowledge of these subjects to which they have been forced to give the greater part of their years of school life. This fact should serve as a warning to the teachers who are occupied with mathematics and physical science in schools, and lead them to the use of methods and practices which will encourage their pupils to apply their knowledge daily to the affairs of common life and business.

The question how the student of chemistry can be brought into the service of industry most advantageously has still to be answered. We may suppose that it is agreed that the young chemist, equipped with a full knowledge of theoretical chemistry and well practised in all the analytical and other operations of the scientific laboratory, requires an elementary knowledge of engineering, and of the properties of materials for construction used in the works, before he is qualified to take charge of operations on a manufacturing scale. This is a kind of knowledge which can be acquired to a certain extent at college, but experience of operations on a large scale is still desirable and the question arises how he is to get it.

In the German and, to some extent, the American works a system has prevailed for many years which seems to have the double merit of being reasonable and practically successful; this system is now being adopted by at least one large chemical concern in Great Britain. Over each department an experienced scientific chemist presides. When an assistant is required a graduate of one of the universities, recommended by the professor under whom he has worked, is engaged under a contract to serve for a term of years at a salary which is modest, but which is sufficient to enable him to live till promotion comes. The first year or two is devoted to learning, under the direction of the chief, the business of that part of the works into which he has been admitted, and the assistant is not expected at first to do more than make himself thoroughly competent in routine work, at the same time the degree of diligence and ability shown determines the rate at which he may look for advancement in pay and position. There is usually a clause in the agreement which forbids the employé to leave this employment and enter the service of another firm in the same business within a certain distance. Men who enter the chemical works under these conditions, however, are not prone to wander, and the prospects for a man of real ability are satisfactory or even brilliant. Unfortunately no system of this kind has become general or even frequent in this country. Too often the manufacturer looks for practical results impatiently, and does not realise the fact that a chemist may have a full knowledge of his subject from one point of view but has to apply that knowledge to problems with which he has no previous acquaintance, also that discoveries cannot be made to order. It is only necessary to know a little

of the history of chemistry and its applications to be aware that experiments carried on for many years by clever men do not always lead to a successful result.

Another method by which university graduates can be made acquainted with the problems of industry, and incidentally one enabling manufacturers who do not choose to establish on their own premises a scientific laboratory and staff may obtain assistance in their endeavour to improve processes, to overcome difficulties or irregularities in existing processes, or to test new ones, may be found in the proposal to institute industrial fellowships. This idea was inaugurated in 1912 by the late Professor Kennedy Duncan chiefly in connection with the University of Pittsburg, in the United States, and is now known by the title of the Mellon Institute for Industrial Research.

The plan is as follows: any manufacturer desiring skilled assistance may apply to the Institute for a chemist qualified to prosecute research. The chosen person, nominated by the Director, is provided with a separate laboratory and with necessary materials, together with facilities for large scale experiments provided by the manufacturer. The latter also provides the remuneration payable to the Fellow for one or more years. The Fellow works under the general supervision of the Director of the Mellon Institute, and through him periodical reports on the progress of the work are forwarded to the employer. Any discoveries made by the Fellow during the tenure of his Fellowship become the property of the employer, subject to the payment of royalty or other consideration, the amount of which is determined by the Board of Arbitration provided for in the Scheme.

Many other details are considered and arranged in the programme, which appears from the reports published annually to have met with remarkable success during the twenty odd years it has been in operation. In spite of the recent industrial depression in the United States the scheme has been well supported, and over two hundred skilled investigators are now being subsidised by some seventy industrial firms. There appears to be no reason why this plan should not be adopted in many other universities, as it could manifestly be put into operation in all those cases in which direct daily observation of processes going on in the works is not essential. That is the qualification which seems to indicate a greater convenience in the other system,

previously described, in which the chemist in the laboratory has immediate access to the manufacturing operations, for the advantage of which he is supposed to be at work.

From what has been said it must not be imagined that manufacturers in Great Britain have not undertaken a considerable amount of research work, but it is difficult to estimate its extent. Obviously the results, if any, are reserved for private utilisation, but whatever has been accomplished the necessity for work of this kind is as yet far from being recognised by manufacturers generally. The introduction of new principles and processes founded on them must have been preceded by enquiry and experiment by competent workers. The wide application of electricity for the production of high temperatures and in electrolytic operations, the use of catalytic agents, as in the contact process for sulphuric acid, the hydrogenation of fats and oils, and several other chemical manufacturing operations which have actually been established in England during the last few years, give evidence of advances which have been accomplished and which give proof of the application of physics and chemistry. There are, however, so many other directions in which this country is dependent for supplies from other countries that much more remains to be done.

Sufficient has now been said to convey a general idea of the position of chemistry as the basis of a calling or profession. In the chapters which follow a description will first be given of some chemical laboratories, which may be regarded as typical, and of the more important operations which are carried on in them, in order that the reader who is not a chemist may gain some notion of the work carried on in the scientific laboratory and in the chemical manufactory.

Chemistry is that department of natural knowledge which is concerned primarily in determining composition, or in other words finding out what things of all kinds are made of. The chemist has to deal with gases like common air, with water and other liquids, and with solid matters of all kinds whether mineral or organic. He is therefore not confined to the study of composition only, but, with the aid of methods and instruments drawn from other departments of science, he examines the properties of bodies and the conditions under which compounds are formed or are decomposed. In every operation of nature chemical change is incessant, in the material of the earth's crust,

in the sea and in the air, in life, death, and decay. The chemist has all nature for his province.

By careful study by many generations of men, more particularly during the last century and a half, knowledge has been substituted for ignorance, system for chaos, and a body of theory has been established which enables the chemist to classify the multitudinous facts of nature and so render them more or less intelligible. The application of specialised portions of this knowledge to manufacture provides mankind at the present day with many of the conveniences of modern life which could never have been dreamed of by our ancestors.

The later portion of the book will contain an account of the most important discoveries which not only find practical applications, but give entirely new views of the constitution of the world in which we live.

PART I
CHEMICAL LABORATORIES AND THE WORK
DONE IN THEM

CHAPTER II

LABORATORIES AND THEIR USES

THE word *laboratory*, which merely signifies a workshop, has by long custom been applied chiefly to the room or building in which chemical experiments are carried on, or at any rate experiments in natural science in which operations more or less chemical in character are practised.

The chemists of the past were content with very modest accommodation, provided a sufficient amount of light was secured together with a supply of water and the means of obtaining heat. Berzelius, the famous Swedish chemist, who lived till 1848, carried out the greater part of his accurate estimations of atomic weights as well as other researches in a room communicating with the kitchen of his house, where Anna his servant maid acted as his only assistant.

At this time the teaching of chemistry in the universities was everywhere conducted solely by the method of lectures which were rarely enlivened by experimental demonstrations. The student desirous of learning something of chemical analysis or other practical chemical work had to seek the privilege of admission into the private laboratory of some professor of chemistry. Liebig tells us that he had to leave his own country, Germany, where in his youth there were no chemists of any importance, in order to apply to Gay-Lussac in Paris for permission to work under his direction. With this experience in his mind it is not surprising that on his return home two years later he should have determined to found in his own country an institution in which students could be instructed in the art and practice of chemistry, in the use of chemical apparatus, and the methods of chemical analysis. Such was the origin of the famous laboratory at Giessen which, from 1824 onwards, for many years attracted students from every civilised country. It was but a modest place with none of the appliances with which we are now familiar.

It was twenty years later before a laboratory for instruction in chemistry was opened in this country, and even then it was not either Oxford or Cambridge which took the lead in this important reform.

The first laboratory in this country opened for the use of students of chemistry was provided by the Pharmaceutical Society of Great Britain at their premises in Bloomsbury Square. In 1844 places were furnished for twenty-one students. The laboratory was a single apartment, the ventilation of which was very imperfect, and as many of the operations required the use of coke furnaces the place was full of smoke and fumes. Almost immediately after this the Royal College of Chemistry was founded, and for the first year or so carried on operations in George Street, Hanover Square. It was then transferred to its permanent home in Oxford Street, where a building had been provided which still exists, and, with an additional upper storey, contained the offices of the General Medical Council. The building had a frontage of only 34 feet with a depth of 53 feet.

The whole of the first floor was occupied by the Students' laboratory, while on the ground floor were a private laboratory for the Professor, a balance room, and a lecture room at the back. The basement contained furnaces and a steam-boiler and stores.

It is unnecessary to pursue this retrospect any further, for the example set at Giessen, when once the movement had begun, was followed in all the great centres of instruction. But even the new laboratories were very inferior in size and equipment to those which have been erected in more recent times.

The rate of progress during the last thirty or forty years has been very rapid, and, stimulated by the rivalry between nations and by the rapidly increasing numbers of students seeking instruction, the buildings provided for the accommodation of the chemical departments in the universities and modern colleges as well as the numerous technical schools have gradually assumed more and more palatial features. The first important step in this direction was taken by the German Government, when, after the Franco-Prussian war in 1870-71, Strassburg became a German town.

Possibly animated by the desire to placate the Alsatian population, splendid separate institutes were erected in Strassburg to provide for the several branches of science, chemistry,



FIG 1 —MICROSCOPE ROOM, BREWING DEPARTMENT
UNIVERSITY OF BIRMINGHAM



FIG 2 —BREWING DEPARTMENT, UNIVERSITY OF BIRMINGHAM

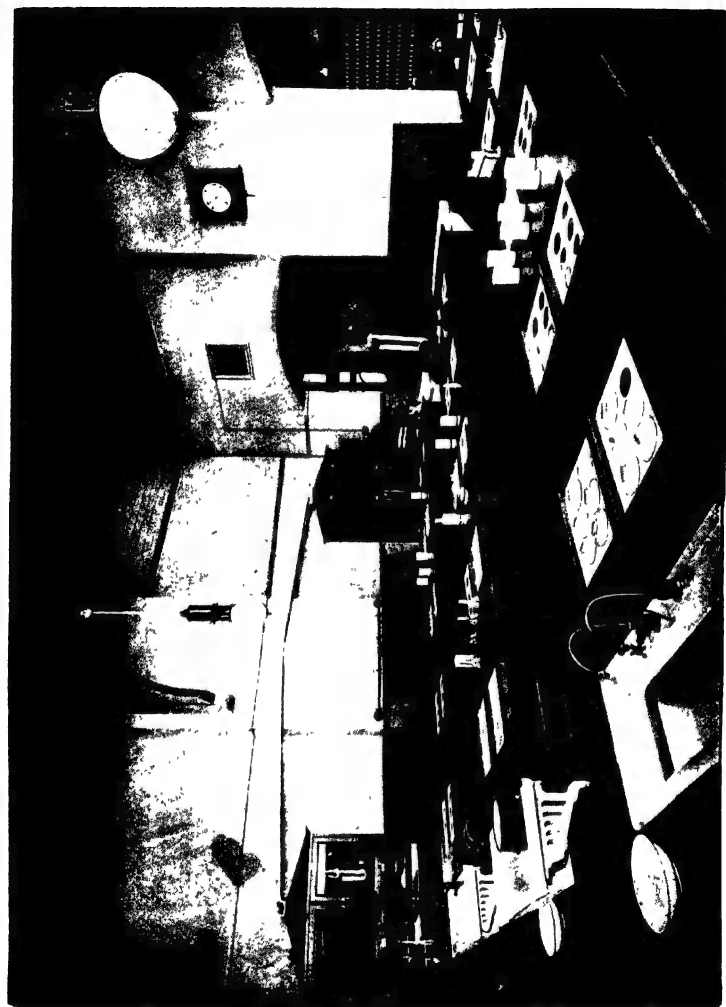


FIG. 6. COURTYARD OF TECHNOLOGY, MANCHESTER

botany, geology, etc. Each of these institutes contained accommodation, on a scale previously unknown, for laboratories, lecture rooms, and museums, as well as residence for the chief professor. Even the Strassburg chemical institute is now surpassed in dimensions and outfit by some of the establishments more recently erected in various parts of the world.

Before proceeding further it will be convenient to review the purposes for which the very numerous chemical laboratories have been erected in all the civilised countries of the world. In the first place it must be remembered that they are not all devoted to the purposes of instruction. Many are occupied with purely practical objects in connection with analysis of products for control of quality, or for fiscal purposes, or in association with manufacturing operations. And in these later times the importance of research is becoming so generally recognised that institutions have been founded and endowed with the sole object of providing facilities for carrying on such work independent of teaching, on the one hand, and of industrial or practical purposes on the other. The following classification of laboratories must be understood to be only illustrative; the total number of universities and of technical schools in Britain alone is very large, and any attempt to enumerate completely even these would require a volume to itself. The reader must be informed therefore that if the universities of this and other countries, and such famous technical schools as the Massachusetts Institute of Technology at Boston, are not included in the analysis it is from no want of sense of their importance.

I.—LABORATORIES FOR INSTRUCTION

1. Universities and University Colleges.

Special Departments for Agriculture; Brewing; Dyeing; Fuel; Glass; Leather; Metallurgy; Textiles.

2. Technical Colleges.

Among the more important, which are of university rank, are: The Imperial College at South Kensington; The Royal Technical College, Glasgow; The Municipal School of Technology, Manchester; The Heriot-Watt College, Edinburgh.

3. Agricultural Colleges.

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4. Public, Technical, Secondary and Elementary Schools.

The laboratories in some of the great public schools of England are now as well equipped as those of the universities.

II.—LABORATORIES FOR ANALYSIS AND PUBLIC SERVICES

1. Government Laboratories.

Central; Admiralty; Woolwich Arsenal; Imperial Institute.

2. Public Analysts.

3. London County Council.

4. Many private analytical.

III.—LABORATORIES CONNECTED WITH MANUFACTURES

These are private establishments connected with individual works for the production of iron and steel and metals generally, also with alkalis and acids, drugs, dyes, and chemical products of all kinds; many of these laboratories have active research sections.

IV.—LABORATORIES FOR RESEARCH ONLY

The Royal Institution, established under Royal Charter 1800.

With it is associated the Davy-Faraday Laboratory, founded and endowed by the late Dr. Ludwig Mond.

The Lister Institute, corresponding in aims with the Pasteur Institute in Paris.

Establishments of the Department of Scientific and Industrial Research, such as the National Physical Laboratory, the Chemical Research Laboratory, the Fuel Research Station, and the Food Investigation Laboratories.

Industrial Research Association Laboratories, one of the most important being that subsidised by the Cotton Industry, at Didsbury, Manchester.

The Lawes Agricultural Trust. Experimental Station and Laboratories, Harpenden, Herts.

In the following pages will be given some description of the work carried out in, and in some cases the general arrangement of, laboratories representing examples of each of the four types

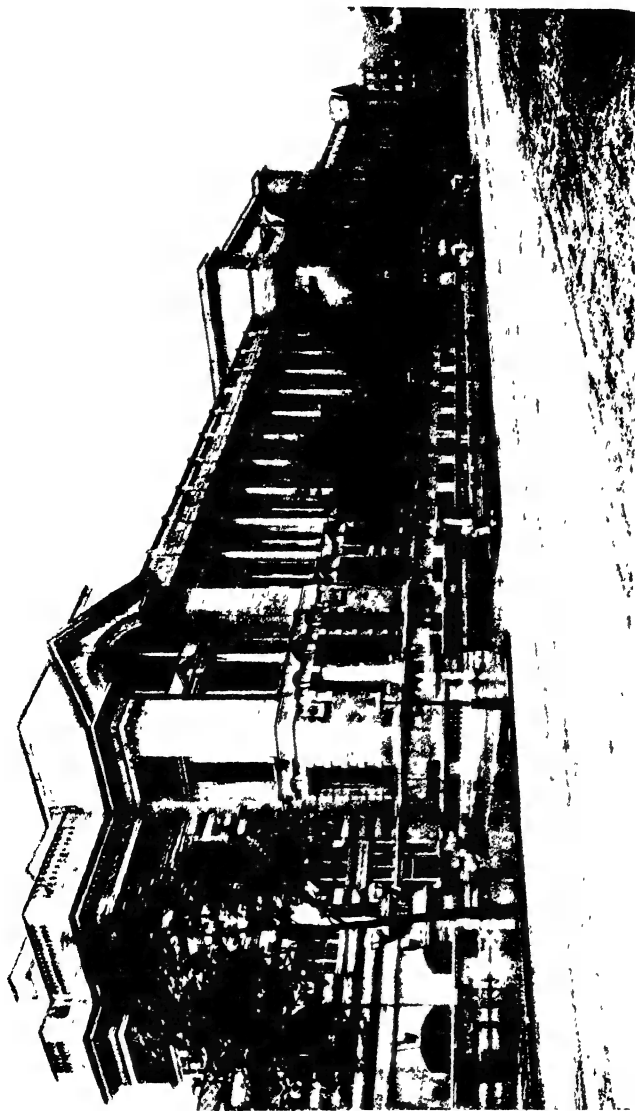


FIG 4 —IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON
DEPARTMENTS OF CHEMISTRY AND PHYSICS

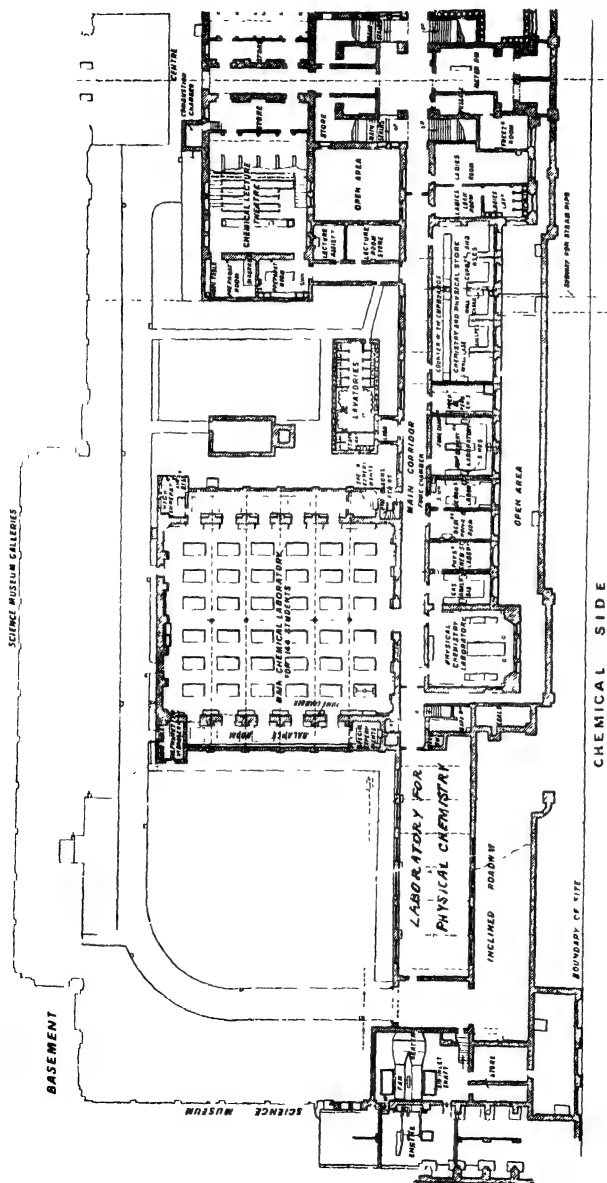


FIG 5 —BASEMENT

just enumerated. They are not by any means the only large and well-equipped establishments in Great Britain, but they will give the reader a good idea of the institutions in which the chemist receives his training and in which he subsequently carries on his profession, as well as indicating the type of work he is called upon to carry out.

I.—THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON

One of the largest and most completely equipped chemical departments was erected by the British Government for the accommodation of the Royal College of Science and Royal School of Mines at South Kensington, London, and was occupied for the first time in 1906. The architect of the building was Sir Aston Webb, R.A., but the arrangement and fittings of the interior were designed by the then professor of chemistry, Sir William Tilden.

A general view of the exterior of the principal building is shown in Fig. 4, from which it will be seen that it consists of a central block with two wings. The eastern half of the building is devoted wholly to chemistry, while the western half is occupied wholly by physics. The central mass contains the entrance and stairs leading to upper stories occupied by the Science Library which forms a part of the South Kensington Science Museum. This provision for pure chemistry is supplemented by the Department of Chemical Technology (and Fuel), of which the separate building has been more recently erected and occupied for the first time in 1915. The College and the School of Mines are now united, together with the City and Guilds of London Institute, into one chartered body, the Imperial College of Science and Technology.

The buildings contain complete suites of laboratories, lecture rooms, and accessory apartments, with accommodation for the teaching staff in the four divisions of

1. Physical Chemistry.
2. Organic Chemistry ;
3. Inorganic and Analytical Chemistry ;
4. Chemical Technology.

There is a professor at the head of each division, with a number of assistants.

As the internal arrangements are typical of what is aimed at in many chemical institutions it will be worth while to glance at the plans of the several floors which are shown in Figs. 5, 6,¹ and 7, which show respectively the basement, the ground floor, and the first floor.

From the main entrance stairs descend on the left to the lower ground floor, upon which level are found the chief lecture theatre, the large chemical laboratory, with separate places for 144 students, and the series of laboratories for physical chemistry. The balance rooms for the big laboratory extend along each side of the building, access being provided at five points on each wall. The lecture theatre provides comfortable sitting space for 150 students, but there is a large floor at the back and considerable room in front, so that about twice that number of auditors can be provided for when occasion requires. At the back of the table are blackboards, means of hanging diagrams, and two screens for projected pictures or lantern views of experiments. There are several wide pipes leading downwards from the surface of the table by which even copious fumes can be sucked away and prevented from reaching the audience. There are also numerous connections, visible in the picture, by which water, gas, electric current, and vacuum can be at once utilised for experiments to be shown on the table. The room can be rendered completely dark, when necessary, by the provision of black blinds to all the windows.

In addition to these there is a spacious store for physical and chemical apparatus, of which a large quantity in the form chiefly of glass flasks, beakers, and other necessary vessels is always kept in stock. Close at hand is the freezing room, in which there is a machine, electrically driven, for the production of liquid air.

Ascending to the floor above there is a series of apartments which provide a lecture room with seats for about fifty students, a library of reference furnished with the principal chemical periodicals, dictionaries, and other large special treatises. Adjoining this is the private room for the professor of physical chemistry, and a small laboratory, where there is room for about eight or ten workers.

The floor above, called the first floor, is occupied almost entirely by the department of organic chemistry.

¹ The section in this plan marked "administrative offices" is now occupied by the department of Physical Chemistry, mainly for research work.

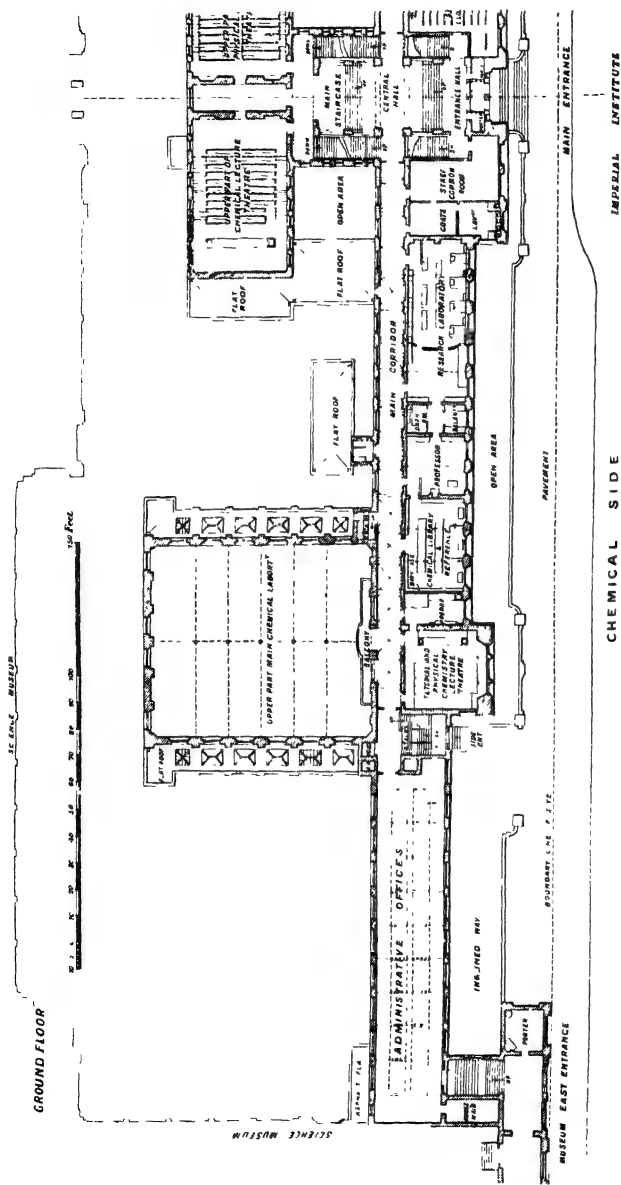


FIG 6.—GROUND FLOOR

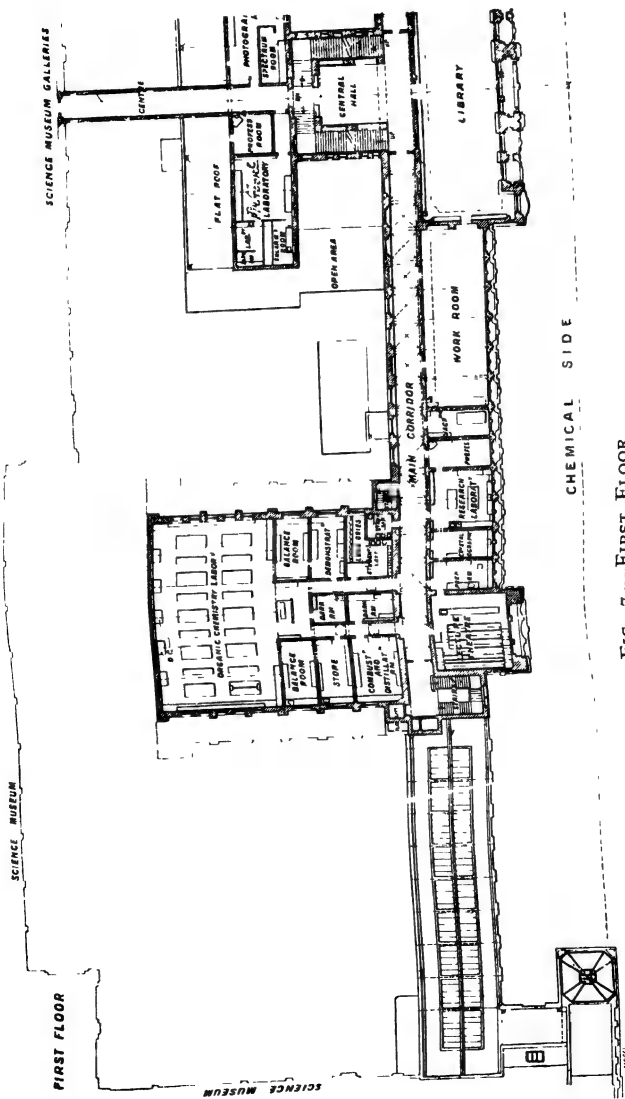


FIG. 7 — FIRST FLOOR

The laboratory devoted to organic chemistry is over the large laboratory depicted (Fig. 9), and occupies about half its area. The fittings here differ somewhat from those below, as it is necessary to give each student a larger share of space and to provide for certain operations not usually practised in the general laboratory. The organic chemistry laboratory therefore provides for only forty workers. The other half of the space contains rooms for the demonstrator, for balances, for stores, and for special operations, such as combustions and distillation of very volatile liquids such as ether. There are also ten small research rooms.

The top floor is occupied by the advanced laboratory, with places for one hundred students, half of whom face each way toward the desk of the presiding demonstrator. A supply of balances is found at each end of this laboratory, and there are several rooms for special operations, such as water analysis.

The three illustrations (Figs. 8, 9, 10) afford views of the interior of the largest of the laboratories and of the chief lecture theatre.

The reader who is not a chemist will require some further information as to what is to be found in such establishments as those just described, and what sort of work goes on therein.

Returning therefore to the main laboratory in the pure chemistry department, it will be seen from the picture that the working benches are arranged in groups of four over the entire area. Each student is provided with a share of the table top, five feet from side to side, a sink on one side, and a suite of drawers and cupboards below, which provide for all ordinary requirements. On the top of the table and in front of the worker are shelves on which stand bottles containing the liquid and solid reagents most commonly in use. There are two gas taps to which the Bunsen burners employed can be attached by flexible rubber tubing. The water supply is also duplicated, the one tap serving for the washing of glass or other apparatus, while the other is permanently connected with a high pressure water pump, by which a reduced pressure or "partial vacuum" may be established in any vessel connected with it. This is especially useful in hastening filtration through the paper filter commonly used.

So much for the special accommodation provided for the student individually. But everyone has access also to the further arrangements for common use.

In so large a laboratory it is necessary to consider the distance to be traversed in reaching the balances and larger fume chambers. In order to reduce this as much as possible these are distributed along the two sides so that no student requires to walk further than half the width of the laboratory for such purposes. Spacious fume chambers and doors, leading directly into the two long balance rooms, are to be found alternately the whole length of the room. The fume chambers are glazed on all sides except the back wall against which they are placed. Each is fitted internally with gas and steam pipes, having cocks at suitable intervals, so that all sorts of operations in which fumes are evolved, or evaporation is required, can be conducted. Water taps are also to be found in them, so that condensers used in distillation can be kept cool, and at the back of each chamber is a shallow groove or trough cut in the slate floor of the chamber so as to carry off the water to the drain.

In the laboratory itself are also provided apparatus for the condensation of steam and production of distilled water, which is another indispensable material necessary in all analytical work and in a great many other chemical operations. In connection with the distilled water apparatus are several copper ovens, heated by the entering steam, which serve to dry any materials placed within.

The laboratory is lighted by electricity, one lamp being placed over each working place, while clusters of five are hung from the ceiling for the purpose of general illumination.

The average floor space for each worker is nearly 50 square feet. It may be added that the floor is covered with wood blocks set in concrete, and immediately beneath and easily accessible are channels in which gas and water pipes, etc., are laid, as well as open troughs by which the waste liquids from the sinks above are delivered into the drain. Obstructions resulting from the accumulation of solid matters in pipes are thus avoided.

In the laboratory for organic chemistry the chief modification in the arrangements of the working tables is in the direction of giving more space to each student. Instead of 5 feet from side to side as in the analytical laboratory, 7 feet are allowed, and between each block of work tables there is a narrow operation table, covered with lead, and supplied with gas, water, and steam taps. Here distillations may be conducted as well as any other

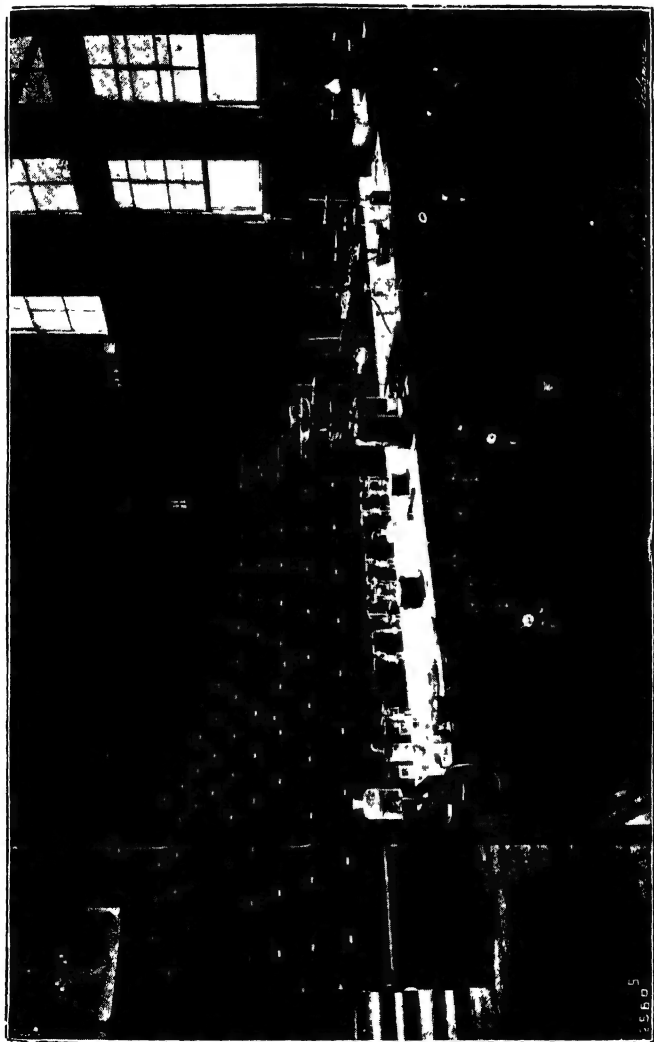


FIG 8.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON
CHEMICAL LECTURE ROOM

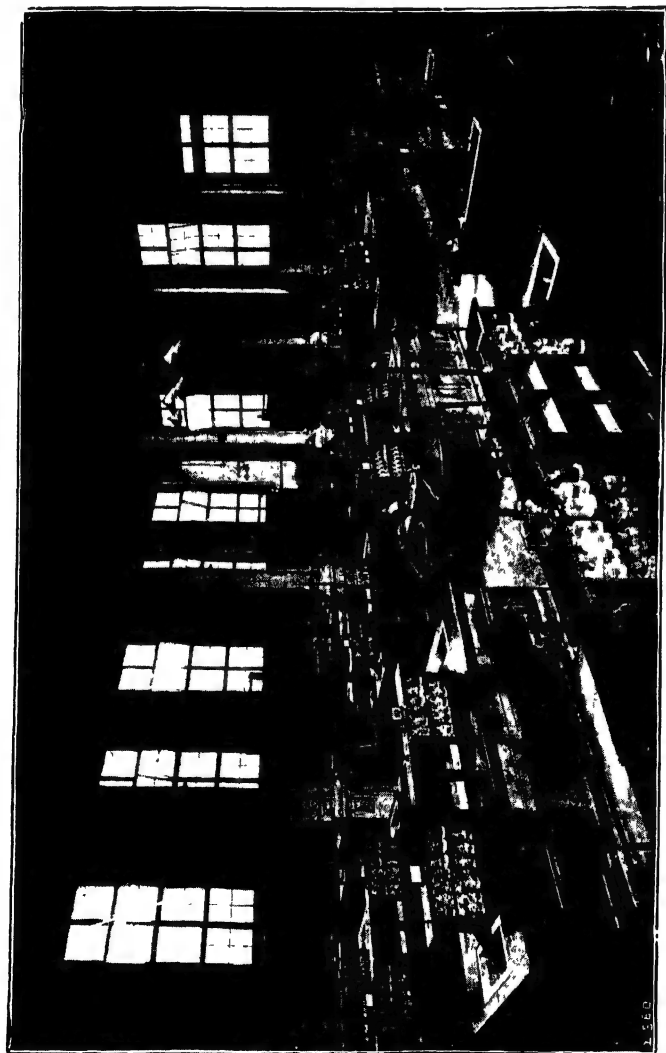


FIG 9 — IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON
MAIN CHEMICAL LABORATORY

operation which requires an extended train of apparatus. The operation table has a raised edge so that in the event of accident any liquid spilt will not run to the ground, but may be swept down a central channel to the drain. This is necessary in view of the fact that volatile and inflammable liquids are so frequently used in this class of work.

The fume chambers in this room are similar to those in the other laboratories, with the addition of cupboards below closed by sliding iron doors. In these spaces are placed the iron boxes in which sealed glass tubes can be safely heated. If an explosion occurs from the bursting of one of these tubes no damage will be done.

In addition to the main laboratories described there are a considerable number of small laboratories for research in physical, inorganic, and organic chemistry. A special room is devoted to agricultural chemistry, and the analysis of foods and drugs is studied in three laboratories specially equipped for the appropriate chemical and microscopical analysis. The Whiffen laboratory, equipped mainly as a result of the generosity of a past student, W. G. Whiffen, Esq., is fitted with semi-large scale plant, so that students can learn to conduct processes on something like the manufacturing scale. It is also of value when large amounts of a particular substance are required.

The laboratories just described were designed for instruction and research in pure scientific chemistry. A very large amount of work of this kind has been done in them with results which have been communicated chiefly to the Chemical Society of London, but a good deal has also been done in connection with problems of a more or less directly technical character. To add to the facilities already provided in this direction the building in the neighbouring Prince Consort Road provides for the Department of Chemical Technology, having three sub-departments, namely, the study of fuel—solid, liquid, and gaseous; chemical engineering, that is, the design and working of chemical plant for industrial purposes; and special electro-chemistry.

The buildings at present provided form part of a plan which would ultimately include a building with a front and two wings, leaving a space between the wings large enough to allow of the erection of temporary buildings for special technical researches.

The present equipment of the department of Chemical Technology is designed for study and research in the following

subjects : analysis and investigation of various types of fuels ; gaseous combustion and explosions under high pressures ; the study of flame ; the measurement of high temperatures ; refractory materials ; industrial catalysis ; blast furnace processes ; reactions in the electrical discharge ; and the design of chemical plant.

A valuable addition to the department of fuel is the experimental gas producer plant presented to the college by Mr. Robert Mond. The plant consists of a producer with the type of grate introduced by the late Dr. Ludwig Mond, and from this the gas is directed through washing towers and scrubbers, so arranged with valve control that any degree of scrubbing can be given that is required. The gas then passes through a tar extractor, and finally through a sawdust scrubber to the gas-holder, which has a capacity of 3000 cubic feet.

Other special apparatus worthy of mention are the intermediate-scale equipment for the distillation of petrols, tar, fuel oils, etc. ; the high-speed cameras for the photography of rapidly moving flames ; and apparatus for the study of gaseous explosions at pressures up to 1000 atmospheres.

The department of fuel, etc., has been designed and arranged by Professor W. A. Bone, and contains much gas apparatus and other devices connected with his well-known researches on combustion.

II.—THE GOVERNMENT LABORATORY, LONDON

The following account of the history and work of the Government Laboratory is extracted from Reports of the Government Chemist, issued annually, and published by H.M. Stationery Office. They contain much interesting information as to the nature of the enquiries which have to be made in such an institution as to the quality of foodstuffs and various beverages supplied to the public, the testing of alcoholic liquids and tobacco for the purpose of levying duty, the investigation of various questions which arise from time to time in relation to public health, such as arsenic in beer, and lead in the glazes of pottery and china ware, and the supply of materials for the public services.

The figures given as to the number of samples analysed attest the activity of the Government Chemist and the large staff of skilled workers under him.

A review of the work done in the laboratory also gives a fair

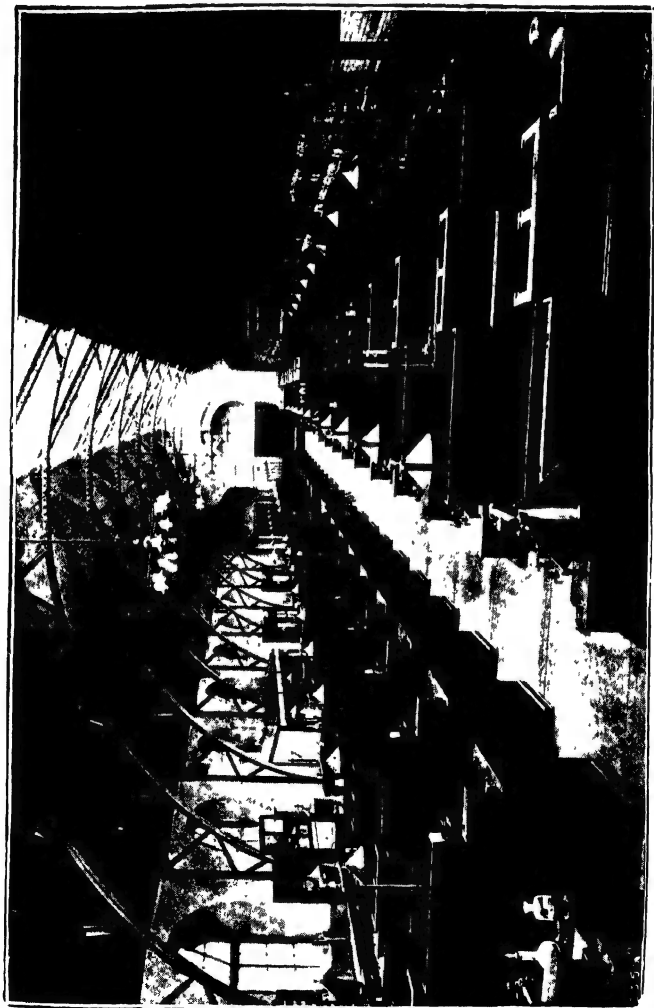


FIG 10—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON
ADVANCED CHEMICAL LABORATORY

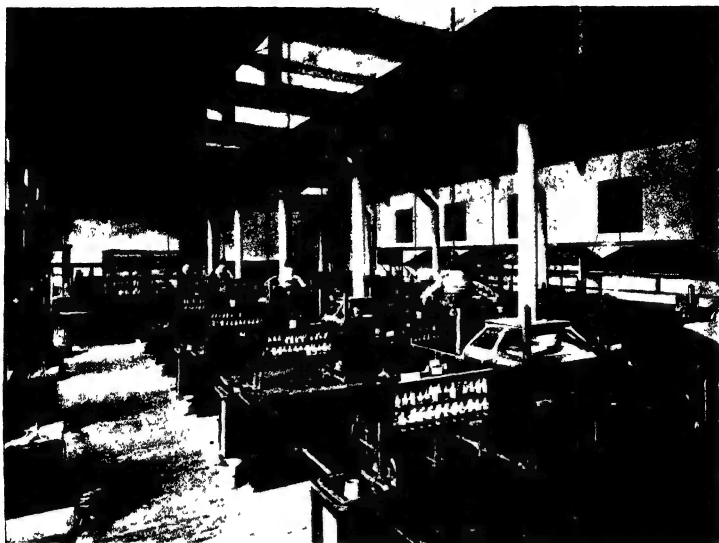


FIG. 11 —CHEMICAL LABORATORY, SYDNEY UNIVERSITY



FIG. 12 —ASSAY ROOM, SYDNEY UNIVERSITY

idea of the multifarious character of the business undertaken by the Consulting and Analytical Chemist generally, and of the officials known as "Public Analysts" throughout the country.

The origin of the Government Laboratory dates back to 1843, when a laboratory was established at Somerset House in connection with the Inland Revenue Department, mainly for the purpose of checking the adulteration of tobacco. The scope of this laboratory was afterwards extended so as to include the analysis of almost every excisable commodity.

A laboratory was also established at the Custom House in connection with the Customs service for the analysis of articles liable to duty on importation.

In 1894 the two Revenue Laboratories were placed under one Principal, and from that time were known officially as the Government Laboratory. Each branch of the laboratory, however—Excise and Customs—remained, as formerly, subject to the administrative control of the department with which it was immediately connected, and this anomalous state of things continued until the amalgamation of the Customs and Excise Services in 1909.

While the laboratory at Somerset House was established primarily to assist the officers of the Excise Department of the Inland Revenue in the performance of their duties, other Government Departments obtained the permission of the Treasury to avail themselves of the services of the "Somerset House" chemists. This larger sphere of usefulness was gradually extended until in course of time the laboratory came to undertake work for nearly every department.

By the Food and Drugs Act of 1875 the chemical officers of the Inland Revenue were made the official referees in disputed cases under the Act, and provision was made for the examination of tea on importation, by persons to be appointed by the Commissioners of Customs. At a later date, the principal of the laboratory was appointed Chief Agricultural Analyst by the Board of Agriculture in connection with the administration of the Fertilisers and Feeding Stuffs Act.

With the growth of the demand on the part of the various Public Departments for advice and assistance in matters involving chemical knowledge, it became apparent that the arrangement under which the staff of the Laboratory was composed entirely of Revenue Officers appointed by and subject to the

authority of the Commissioners of Customs and Excise was no longer a satisfactory one. With the view, therefore, of placing all Departments on the same footing as regards the use of the laboratory and of promoting the centralisation, as far as practicable, of Government chemical work, the Treasury intimated, towards the end of 1910, its intention of asking Parliament to provide for the expenses of the laboratory under a separate vote as from April 1st, 1911.

The new department thus constituted is known under the official title of "The Department of the Government Chemist."

The change in administrative arrangements was accompanied by important changes in the method of staffing the laboratory.

As has already been stated, all posts on the staff of the laboratory were formerly filled by Revenue Officers, and there was no avenue by which admission could be obtained to the establishment of the laboratory except through the Customs and Excise Service. While it was generally recognised that there were many advantages to be gained by continuing to employ Revenue Officers on Revenue work, no good reason seemed to exist for confining laboratory appointments to Revenue Officers in so far as the non-revenue work was concerned. It was decided, therefore, on reorganising the staff, to continue to utilise the services of the Revenue Officers for purely Revenue work, but to employ chemists recruited from the open market for non-revenue work.

The established staff of the Government Laboratory consists of the Government Chemist, the Deputy Government Chemist, 6 Superintending Chemists, 11 Senior Chemists, 3 Chemists (Higher Grade), 36 Chemists, 7 Assistants II, and 27 Assistants III; there are in addition a number of Laboratory Assistants, both established and temporary, making a total of over 180.

The duties performed by the staff of the Government Laboratory are of a very varied character. They include the analysis of samples in connection with the assessment of Revenue and drawbacks; of stores supplied to Government Departments on tender and on contracts; of dairy produce imported into this country; of samples referred by Magistrates under the Food and Drugs Act, and by the Board of Agriculture and Fisheries under the Fertilisers and Feeding Stuffs Act; and of articles imported under the Safeguarding of Industries Act, and the Importation of Dyestuffs (Restriction) Act. The laboratory staff

also deals every year with a large number of questions referred by Government Departments for advice, and conducts investigations in connection with such references and with the enquiries of Royal Commissions and Parliamentary and Departmental Committees.

The chemical work of the following departments and other public bodies is now carried out wholly or in part in the Government Laboratory :—Board of Customs and Excise ; Admiralty ; Ministry of Agriculture and Fisheries ; Department of Agriculture and Fishery Board for Scotland ; Colonial Office ; Crown Agents for the Colonies ; Foreign Office ; Home Office ; Board of Inland Revenue ; Post Office ; Stationery Office ; Board of Trade ; Trinity House ; War Office ; Office of Works ; Air Ministry ; Ministry of Health ; Ministry of Pensions ; Dominions Office ; Privy Council ; Government of Northern Ireland ; High Commissioners of India and of Southern Rhodesia ; Scottish Department of Health ; Wheat Commission ; and Geological Survey.

The work of the Excise branch of the laboratory, which was originally conducted at Somerset House, having outgrown the accommodation provided for it there, was transferred in 1897 to the present building in Clement's Inn Passage. The greater part of the analytical work is now carried out in the laboratory in Clement's Inn and in the branch laboratory at the Custom House. There are also provincial stations at Bristol, Glasgow, Hull, Liverpool, and Southampton, as well as one at London Docks which forms part of the Custom House Laboratory organisation, for testing work for Revenue purposes.

The total number of analyses and examinations made in the branches of the Government Laboratory during the years ended 31st March, 1913, and 1934 were :

Laboratory.	1913.	1934.
Government Laboratory, Clement's Inn	126,493	233,316
" " Custom House		
Branch	83,009	128,838
Provincial Chemical Stations	145,257	141,438
Total	354,759	503,592

The large increase since 1913 is to be attributed to the extension in the number of articles which have become dutiable under the Safeguarding of Industries, Import Duties, and Finance Acts of recent years. The number of samples analysed during the year 1933-4 was in fact more than 40,000 greater than for the previous year, partly because of the duties on hydrocarbon oils.

The duty on beer brewed in this country is charged on the wort or unfermented saccharine liquid from which beer is produced by fermentation. The specific gravity of 1055 at a temperature of 60° Fah., distilled water at the same temperature being taken as 1000, was used as the standard specific gravity of wort. Technically such wort is said to have a gravity of 55°, and the duty was increased or diminished in proportion to the degrees of gravity over or under 55. Recently the basis of taxation has been altered to 24s. per barrel of beer of gravity up to 27°, and then 2s. per degree above this, although the old standard barrel is probably still retained by brewers. In practice the beer duty is levied on the basis of entries made by the brewers in official books supplied to them by the Revenue authorities. These entries contain a statement of the quantity of materials—malt, sugar, etc.—to be used, and of the quantity and gravity of the wort produced.

For the purpose of assisting the officers in assessing the duty on beer, and as a check on the operations of the brewers, samples of the malt and other materials used in brewing are sent to this laboratory in order that their wort-producing value may be determined, for purposes of comparison with the quantity actually brought to charge. These brewing materials are also examined for arsenic and other deleterious substances in the interest of the public health.

For the purpose of checking the brewers' declarations as to the gravity of their worts, a large number of samples in various stages of fermentation are sent to the Government Laboratory or its branches in order that the original gravity may be determined. During the year 1933-4 beer samples to the number of 43,100 were taken in connection with the assessment of duty, and 4888 for checking purposes; in 176 cases the declared gravity was found to be 1 to 3° low.

With a view to the suppression of the practice of diluting beer, which is prohibited by Statute, numerous samples of

finished beer taken from the premises of publicans and other licensed retailers are examined at the laboratory. Although in the years 1910-11 and 1911-12 about 7 and 6 per cent, respectively, of the samples analysed were found to be so diluted, the number has been steadily decreasing, and in 1933-4 no deliberate dilution of beer by publicans was detected.

The percentage of spirit was determined in 758 samples of herb beers and other imitation beers, beer substitutes, and temperance beverages. In only 19 of these did the amount exceed the legal limit of 2 per cent of proof spirit.

Samples of beer and of brewing materials are regularly examined at the laboratory for the presence of arsenic. The total number of samples tested in the course of the year, including beer, wort, malt, sugar, and other materials used in brewing, was 2029. It is satisfactory to have to record that only 25 of these were found to contain arsenic in slight excess of the limits laid down by the Royal Commission on Arsenical Poisoning, namely, the equivalent of one-hundredth of a grain of arsenious oxide per pound in the case of solids, or per gallon in the case of liquids. In all cases in which the proportion of arsenic is above the limit, efforts are made to trace its origin and to prevent contamination in future.

Cider is obtained by fermentation of apple juice. Beverages of a non-alcoholic character are frequently sold as cider or under names such as "Sparkling Cider" and "Champagne Cider," the words "non-alcoholic" or "non-excisable" being occasionally added. Some of these beverages are mixtures of real cider with solutions of sugar and contain less than 2 per cent of proof spirit. But the great majority of the non-alcoholic ciders, so called, are entirely free from fermented apple juice, and are simply solutions of sugar which have been aerated, flavoured, and coloured. The use of any name for such beverages, which suggests that they consist wholly of fermented apple juice or cider, is an infringement of the Merchandise Marks Act, and samples are examined in the laboratory for the Ministry of Agriculture and Fisheries in the interests of the makers of genuine cider. The duty on genuine cider is charged at the rate of 10 per cent *ad valorem*, unless it contains added sugar or spirit, when it is treated as a preparation containing spirit.

Beverages of this class are frequently prepared from liquids or essences supplied by manufacturers who also furnish a recipe

for making "cider" from them. On one occasion a firm stated that they had prepared a so-called "cider" from a liquid supplied by a continental firm as concentrated apple juice. A sample of this liquid was found to be a strong solution of sugar flavoured with fruit essence and coloured with aniline dye and to be quite free from apple juice.

The earlier stages of the manufacture of spirits and beer are practically the same, and the methods adopted for checking the distillers' operations during the preparation of the fermented liquor or "wash" from which the spirits are distilled are very similar to those employed in the case of beer.

The duty is, however, charged on the spirits actually produced, and the main object of the preliminary checks on the brewing entries is to ensure that the proper quantity of spirits has been brought to charge, having regard to the quantity of materials used and the quantity of wash distilled.

The duty is not usually paid on spirits immediately on completion of the manufacture or immediately after importation, spirits as a rule being stored for shorter or longer periods in duty free warehouses. During storage soluble matter is abstracted from the wood of the casks, and in the subsequent treatment which is required to convert the spirits into gin and other beverages, small quantities of sugar, and of colouring and flavouring matters are added. In these cases and also when dealing with medicinal spirits, essences, and other preparations distillation or other treatment is necessary since the true alcoholic strength cannot be determined directly by Sikes' Hydrometer, the legal instrument used by the Customs and Excise officers for this purpose. A large number of samples of spirituous preparations must therefore be subjected to a more or less detailed chemical analysis before their true strength can be ascertained. Brandy, rum, and other imported spirits and spirit mixtures require similar treatment before the extent to which their true alcoholic strength is "obscured" by the colouring, flavouring, and other matters present in the spirit, can be determined.

Alcohol of high strength is allowed duty free for scientific and manufacturing purposes, and for domestic uses such as burning in spirit lamps. In most cases the alcohol for these purposes is required to be "denatured" or mixed with nauseous or tell-tale ingredients to prevent its consumption as a beverage or its use in medicines or preparations capable of being taken internally.

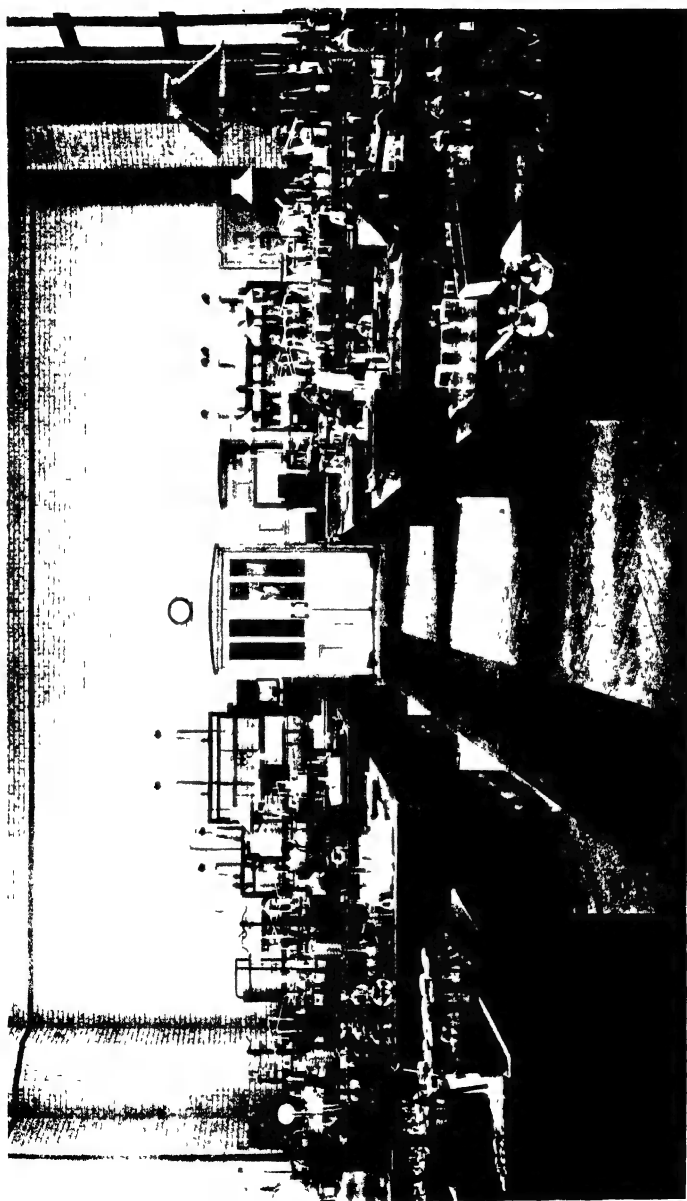


FIG 13—GOVERNMENT LABORATORY CUSTOMS AND EXCISE MAIN LABORATORY

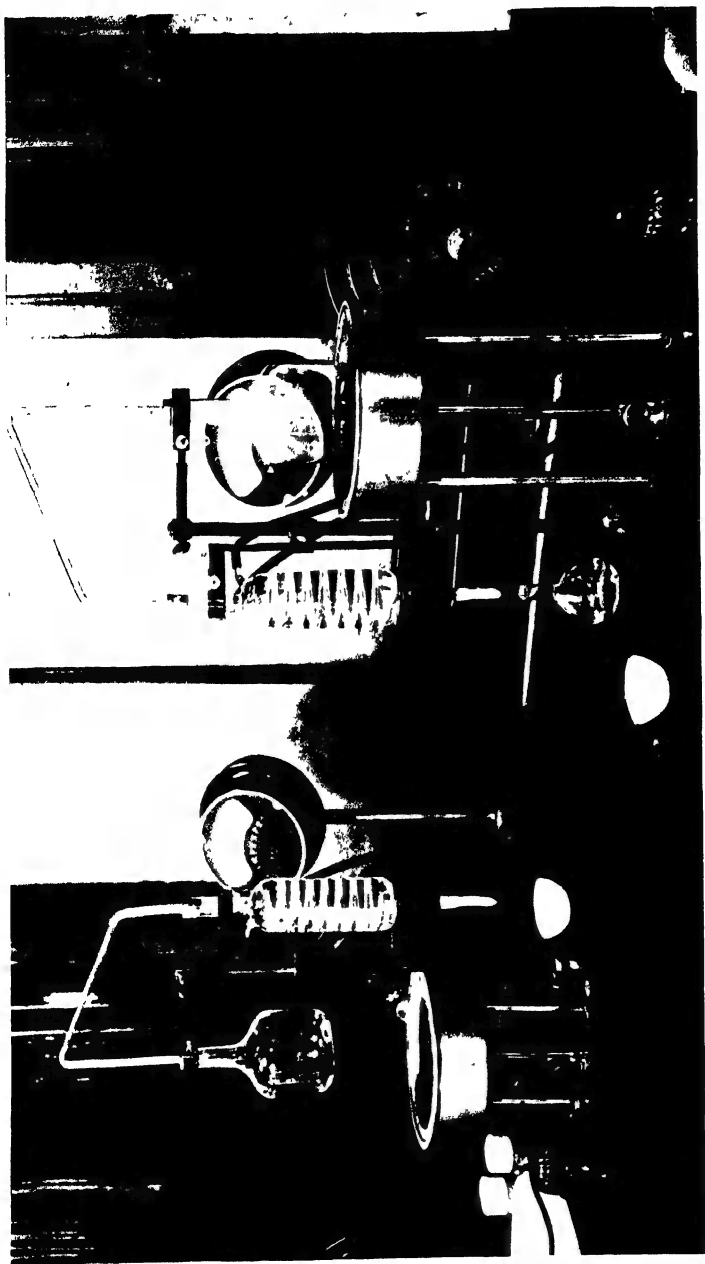


FIG 14—GOVERNMENT LABORATORY ELECTRIC HEATERS FOR WINE AND SPIRIT DISTILLATION

“Mineralised methylated spirit” which is allowed to be sold retail is ordinary alcohol denatured with a mixture of 10 per cent of wood spirit and three-eighths of one per cent of mineral naphtha. “Industrial methylated spirit” is ordinary alcohol denatured with half this quantity of wood spirit without mineral naphtha. The latter spirit can only be used for manufacturing purposes under regulations approved by the Commissioners of Customs and Excise. Other denaturants are allowed in connection with particular manufactures. The denaturants in all cases must be submitted for approval to the Government Chemist, and samples are taken frequently during the manufacturing processes in which the spirit is employed, as well as samples of the finished articles manufactured, in order to ascertain whether the conditions imposed are being complied with. Beverages and medicinal preparations in which the presence of methylated spirit is suspected are also examined with a view to the prevention of any illegal use of the denatured spirit.

Fusel Oil, a by-product of the manufacture of spirits, consists mainly of alcohols of higher boiling-point than ordinary alcohol. It usually contains some dutiable spirit, but may be delivered by distillers duty-free provided that the amount of proof spirit does not exceed 15 per cent; this proportion of spirit is also allowed duty-free in imported fusel oil.

Wine imported into this country is subject to Customs duty. In connection with the assessment of these duties, it is necessary to determine the alcoholic strength of the wines imported, and for this purpose many samples are annually examined in the laboratory.

During the year ended March 31st, 1934, 86,885 samples of foreign wine were tested as to their alcoholic strength as compared with 79,942 in the previous year. The great majority of the samples consisted of the lighter varieties containing less than 27 per cent of proof spirit. In no case did the strength exceed the 42 per cent limit.

Foreign or British wines so medicated or mixed with drugs as to entitle them to be classed as medicines rather than beverages may be sold by registered chemists and druggists without a licence. In order to ascertain whether they were entitled to this exemption 114 samples of medicated wines were examined during the year. Wine which has become unsound may be delivered free of duty after the addition of sufficient acetic acid or

commercial vinegar to preclude its consumption as wine. Unfermented grape juice is sampled and tested for spirit on importation. Of 43 samples none was found to contain any chargeable proportion of spirit.

The work of the Government Laboratory under the head of tobacco consists chiefly in the examination of manufactured tobacco for home consumption and of tobacco, commercial snuff, and offal tobacco for drawback ; in the year 1933-4 a total of 84,312 samples were examined.

Samples of manufactured tobacco are examined for the purpose of controlling the amount of moisture and oil, under regulations based on the provisions of the Customs and Inland Revenue Act 1887, as amended by the Oil in Tobacco Act 1900, and the Finance Act 1904, whereby the amount of moisture which may be present in manufactured tobacco is restricted to 32 per cent, and the amount of oil to 4 per cent. When raw tobacco is made into rolls olive oil, or an approved vegetable oil of this class, is allowed to be used to prevent adhesion of the tobacco coils during storing. The use of certain oils for flavouring purposes is also permissible in some circumstances, and sweetening matter can be added in the preparation of certain types of cavendish tobacco.

The officers to whom the duty of inspecting the manufacture of tobacco is entrusted are required to take from each tobacco factory in the United Kingdom one or more samples every week in order to ascertain whether the tobacco conforms to the legal limits as regards moisture and oil. These samples are termed "General" samples. When there is reason to suspect that the limit of moisture or of oil is being exceeded, samples are taken at the factory under such conditions that their identity can be established if necessary in a Court of Justice. The samples so taken are called "Special" samples, and in this category are included also all samples taken from the stocks of retailers of tobacco.

Samples of tobacco are also examined as occasion arises for the presence of ingredients, for example, sugar, liquorice, and colouring matters, the use of which is prohibited by Statute.

In the operations involved in the manufacture of tobacco from the original leaf a considerable quantity of the material is discarded as unsuitable for the preparation of commercial tobacco or commercial snuff. By regulations based on the



FIG. 15.—GOVERNMENT LABORATORY MUFFLE FURNACES FOR INCINERATION OF TOBACCO



FIG 16 --GOVERNMENT LABORATORY ELECTRIC FURNACE ROOM FOR STEEL ANALYSIS

provisions of the Finance Act of 1904, manufacturers of tobacco are permitted to deposit this refuse or offal tobacco on drawback for abandonment, denaturing, or exportation. For Revenue purposes offal tobacco is classified as follows :

1. Tobacco Stalks—the midrib of tobacco leaves.
2. Shorts or Smalls—small pieces of tobacco broken off in the process of manufacture.
3. Offal Snuff—consisting either of ground tobacco or of siftings from tobacco sufficiently fine to pass through the meshes of the official standard sieve.

Some of this offal tobacco is employed in the manufacture of sheep dips, fumigating powders, and nicotine for agricultural and horticultural purposes.

The articles examined under this head included “joggery”—a mixture of tobacco and opium with sugar and molasses—used by Asiatics.

The samples (70,852) examined for assessment of duty on sugar on importation include, besides sugar, articles made with sugar and also those containing glucose, molasses, saccharin, and other sweetening agents. Glucose is largely used for brewing purposes and in confectionery ; molasses in the preparation of foods for cattle and in the manufacture of spirit ; and saccharin in the manufacture of mineral waters and as a substitute for sugar in foods intended for diabetic subjects.

The number and variety of the preparations containing sugar are so great that it has been necessary to adopt fixed rates of duty in the case of those which are imported frequently or in large quantities. The articles so dealt with comprise biscuits, cakes, catsup, chutney, confectionery, condensed milk, crystallised fruit, desiccated cocoanut, drugs, fruit pulp, infants' and invalids' foods, lozenges, invert sugar, jam, milk powder, pickles, and soy. There are, however, many articles for which it has not been found practicable to fix a special rate of duty, and which have therefore to be tested on each importation and assessed with duty according to the percentage of the dutiable ingredients present. Amongst these may be mentioned egg yolk, gelatine, glue, honey, manna, meat extracts, parchment paper, printers' roller composition, and tanning extracts.

Owing to the heavy duty on saccharin, which has approximately five hundred times the sweetening power of sugar, with

a rate of duty in proportion, the inducement to smuggle this article into the country is very great, and numerous ingenious methods devised for this purpose have been detected by the Customs Department. The presence of saccharin has, therefore, to be searched for in all preparations in which there is any probability of its occurrence.

In order to ensure that only genuine tea shall pass into the country all consignments are examined at the ports by tea inspectors appointed by the Commissioners of Customs and Excise under the provisions of the Sale of Food and Drugs Act, 1875. Doubtful samples requiring a more complete examination than is possible by the inspectors are submitted to the laboratory.

Of the 26,978 samples submitted in 1933-4 only 175 were condemned, 88 as containing sand or other foreign matter and 87 as being on other grounds unfit for human consumption. The rejected tea is allowed delivery duty-free for use in the manufacture of caffeine or theine, the alkaloid which imparts to tea and coffee their stimulating properties, and which is extracted for use as a drug. In such cases the tea has first to be denatured under the supervision of Customs Officers to prevent its possible use for human consumption, and samples both of the denatured tea and of the denaturants used are submitted to the laboratory for test to ensure that the process has been effectively carried out.

Coffee is liable to duty on importation and when exported or supplied for use as ships' stores is entitled to an equivalent drawback when not mixed with chicory or other substances.

The coffee substitutes examined in the course of the year were of the usual character, consisting apart from chicory, of caramel, or of roasted cereals, dandelion root and figs; these are charged at the rate of $\frac{1}{2}$ d. duty per $\frac{1}{4}$ lb.

During the year 10,174 samples of chocolate and cocoa were examined for duty and drawback, the duty generally being charged on the basis of fixed rates for regular kinds of imported and exported articles. Liqueur chocolates have also to be examined for the quantity of dutiable spirit they contain.

Under the Act known as the "White Phosphorus Matches Prohibition Act, 1908," which came into force on January 1st, 1910, 59 samples were examined, but in no case was white phosphorus found to be present.

One hundred and thirty-six samples of medicines, or articles offered for sale as medicines, were examined during the year in connection with the Medicine Stamp Acts. These Acts impose duties, payable by means of special stamps, upon preparations advertised for the cure or relief of human ailments. There are, however, certain exemptions, and it is chiefly in connection with these exemptions that analyses of the samples are required. Thus a single medicinal drug, sold unmixed with any other substance, is not charged with stamp duty, and many of the samples received were analysed in order to ascertain whether they were, in fact, simple drugs or mixtures. Another provision of the Acts exempts, in certain circumstances, medicines of which the composition is known, and analyses are required to establish the identity of samples which it is claimed come within this exemption.

Among points of interest which have arisen in the past may be mentioned an instance of pills which were advertised as a remedy for obesity. The magistrate before whom legal proceedings were brought held that obesity was an "ailment" within the meaning of the Acts, and the seller was convicted of an offence. Specimens of water, and of mud compresses, alleged to have radioactive properties and to exert medicinal effects, have been among the samples examined, which included also pills, powders, plasters, ointments, medicinal snuff, herbs, corn cures, embrocations, and various liquid and solid "remedies."

The "Finance Act" (No. 2) of 1931 imposed a duty of 8d. per gallon on hydrocarbon oils, but in 1933 a rebate was allowed on all other than "light oils," although in the Budget of 1935 it is proposed to replace this duty on certain heavy oils. A light hydrocarbon oil, which is in effect motor spirit or turpentine, is defined as an oil "of which not less than 50 per cent by volume distils at a temperature not exceeding 185° C., or of which not less than 95 per cent by volume distils at a temperature not exceeding 240° C., or which gives off inflammable vapour at a temperature of less than 22·8° C. when tested in the manner described by the Acts relating to petroleum." During the year 1933-4 over thirteen thousand samples were examined, many of these being mixed composite articles, such as enamels, lacquers, insecticides and toilet preparations. A number of oils were also examined to determine whether illegal mixtures of kerosene with motor oils were being sold, since it is not permitted to mix

dutiable with rebated oil (e.g. kerosene) except under licence ; five prosecutions in this connection were undertaken, all of which were successful.

Chemical work is performed for the Admiralty in connection with the Contract Department at Whitehall, the Naval Yards, the Engineering Department, the Canteen Inspections, the Hospitals and Schools, and the Medical Branch. The work consists mainly in the examination of food substances, including fresh and condensed milk, butter, margarine, suet, lard, tinned foods, jam, lime and lemon juice, rum, ale and stout, pepper, and baking-powder. It is satisfactory to note that nearly all the samples of dairy produce examined were of genuine character and good quality.

The Public Health Regulations (1925) of the Ministry of Health require the following specifications for condensed milk : Full cream (sweetened or unsweetened) : 31 per cent total milk solids (including 9 per cent milk fat) ; Skimmed (unsweetened) : 20 per cent total milk solids ; Skimmed (sweetened) : 26 per cent total milk solids. The tins must be labelled in a specific form. Of the 124 samples examined by the Government Laboratory during 1933-4 only 9 were reported against ; 7 of these were labelling offences and two were for overstating the quantity of whole milk to which the contents of the tin corresponded.

Under the same regulations 1393 samples of dairy produce and 664 other foods were examined for the presence of excessive amounts of preservative ; 35 were found to contravene the regulations : 31 contained sulphur dioxide, 3 benzoic acid, and 1 contained copper colouring matter.

Samples taken during police raids on opium dens were examined for the Home Office and found to contain hashish, raw opium, prepared opium and opium dross.

The Merchant Shipping Act provides that every foreign-going ship shall carry a supply of lemon or lime-juice and that 1 oz. per day shall be served to every member of the crew after the ship has been at sea ten days, in order to prevent scurvy. By an Order in Council of 1927 orange juice can be used if desired. During the year ending March 31st, 1934, 140 samples of juice were chemically examined and of these 130, representing no less than 15,547 gallons, were approved. Other work for the Board of Trade carried out at the Government Laboratory concerned the examination of condensed milk for merchant ships ; this is

required to contain a minimum of 10 per cent of milk fat, as against 9 per cent for consumption on land.

Among the curiosities of investigation the following duty devolves on the Government Chemist.

Before an Old Age Pension can be granted, it is necessary that the age of the applicant should be clearly established. In the absence of the Registrar-General's certificate, reliable evidence as to age is sometimes obtained from entries of the date of birth in old Bibles or Prayer Books, from names and dates written in books received as gifts in childhood, and from marriage certificates and other documents. Sometimes there is reason to suspect that such entries have been made recently, or that the original writing has been altered for the purpose of deceiving the authorities.

In 1913 at the request of the Deputy Keeper of the Records the composition of a series of mediæval wax impressions of seals of various dates, from the thirteenth to the sixteenth century, was examined with a view to obtaining information for his guidance in devising means for the better preservation of the seals under his charge. Most of the seals were found to consist of mixtures of beeswax and resin, the resin in some cases being ordinary colophony. The wax in the case of two of the seals, dated respectively 1399 and 1423, possessed the character of East Indian rather than European beeswax. An impression of the Great Seal of 1350 was found to consist of pure beeswax, and it is remarkable that the wax, although nearly six centuries old, corresponds exactly in properties with wax of recent origin.

Another example of a curious problem presented to the Government Chemist occurred when sea shells, which had been stored in oak-wood drawers at the British Museum, were found to have become covered with a white incrustation. Investigation showed that the wood was giving off acetic acid, the sour constituent of vinegar, and this reacted with the calcium carbonate (limestone) of the shells to produce calcium acetate of which the incrustation consisted.

In addition to the Revenue and non-Revenue work of the Laboratory and to the special problems presented from time to time, definite researches are often undertaken for various Government Departments; of these there may be mentioned an investigation into the best method for preserving cinema films of

national importance. Work is also undertaken for the International Council for the Exploration of the Sea, and 6054 samples of sea-water were examined in 1933-4 for salinity; one of the objects of this work is to trace the effect of salinity on fish life.

Sufficient has been said to give the reader a general idea of the large number and variety of the problems undertaken by the Government Chemist and his assistants.

III.—THE LABORATORY IN THE WORKS

The business of a works laboratory is, naturally, not general, but is concerned exclusively with the operations actually carried on or in prospect. Hence it is generally divisible under two distinct heads, namely, routine testing or analysis merely for the purposes of control, and, on the other hand, research with a view to improvements or developments. As to the routine work again this relates generally to raw materials bought for manufacture, or products of the factory for the market, or to the testing necessary at several stages of a manufacturing process. The finished products are generally tested so as to see that they comply with the specifications laid down by some standardising authority, such as the American Society for Testing Materials, or the General Medical Council in the *British Pharmacopœia*, by the purchaser, or even by the manufacturer himself. Another kind of work is that which has to be done in order to comply with some legal requirement, such as the Alkali Act, which applies to the escape of corrosive gases from alkali works, vitriol and glass works. Factory effluents are also frequently tested so as to ensure that they do not contain material likely to be harmful to fish life in the rivers into which the effluents discharge.

The testing of the flue-gases passing up the chimneys from furnaces and boilers is an important duty of the works laboratory; from the proportions of carbon monoxide and dioxide present a very good idea can be obtained of the efficiency with which the coal is being burnt. In many works the coal is tested in the laboratory, so that its quality may be determined before being purchased, or an idea of its heating capacity may be obtained prior to actual use.

Raw materials must be analysed not only because they are commonly bought according to a specification as to quality, but their treatment by the manufacturer depends in many cases on

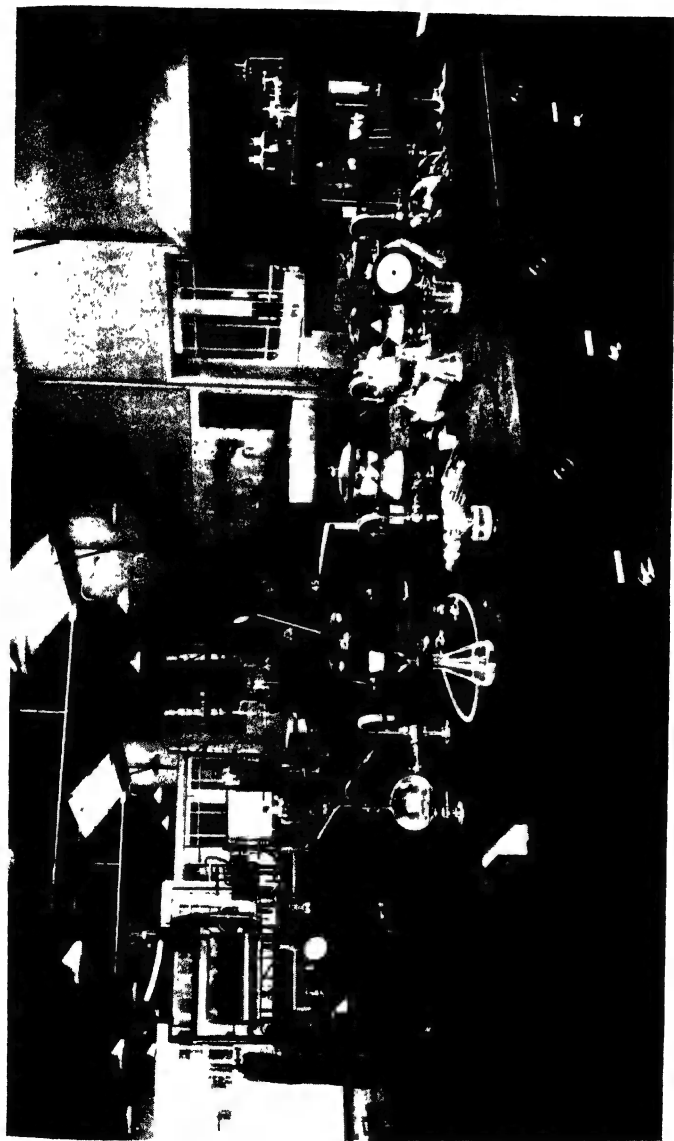
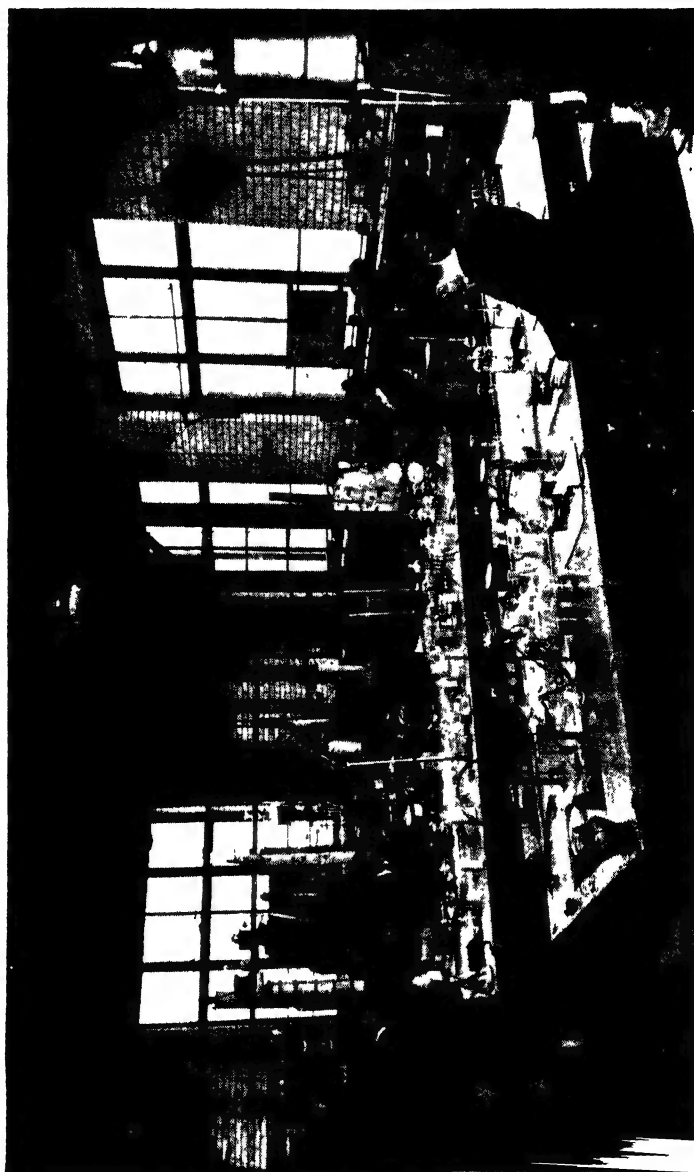


FIG 17—PETROLEUM RESEARCH LABORATORIES, SUNBURY

(By courtesy of the Anglo-Iranian Oil Co., Ltd.)



the amount present of some one constituent or the percentage of one or other of several impurities. Thus the soap-maker must know exactly the percentage of soda in the soda-ash or other alkali he buys; the manufacturer of bleaching powder requires to know the percentage of lime in the material he buys from the lime burner; the dye maker, who starts from benzene, toluene, etc., the hydrocarbons present in coal-tar naphtha, requires to know exactly the percentage of each present in the naphtha obtained from the tar distiller, according as the hydrocarbon is to be converted into aniline, toluidine, etc., the immediate parents of the dyestuff. Raw materials, especially when they are being used for the preparation of medicinal products or of articles of food or drink, are frequently tested for arsenic; this is so often present in the acid used at one stage or another of chemical manufacture that it is likely to find its way into the finished product, unless its proportion is kept low. Reference to arsenic testing has been already made in connection with the description of the work of the Government Laboratory.

The research laboratory, where it is found in connection with chemical works, differs in no important respect from laboratories elsewhere. It contains the usual appliances for weighing, heating, drying, and fittings for reagents, removing noxious fumes and so forth. It must necessarily be provided with the special instruments appropriate to the subjects to be investigated, and should contain or be immediately connected with a good library of works of reference, including some of the principal technical and scientific journals. The research laboratory in the chemical works is much more common to-day than it was twenty years ago, and as will be seen in the descriptions that follow the equipment is often of an advanced character.

In order to give the reader a general idea of the type of work done in works laboratories the organisation at two entirely different types of factories, one making dyestuffs and the other engaged in the manufacture of fine chemicals and drugs, will be described. Although these are probably the best of their kind in the United Kingdom they represent a standard which is being generally approached in other factories.

BRITISH DYESTUFFS CORPORATION (IMPERIAL CHEMICAL
INDUSTRIES LTD.) LABORATORIES

The striking progress, since the war, of the dyestuffs industry, to which reference is made in a later chapter, has only been achieved as the result of much investigation by the chemist in the laboratory, in the works and in the dyehouse, and in order to maintain and improve the position and to serve the many users of dyes to the best possible advantage, there must be no slackening off in the work of the dye-chemist. Some indication of the laboratory organisation of the dye industry and of the type of work done is given in the following account of the chemical department connected with the British Dyestuffs Corporation works at Blackley, Manchester, under the control of Imperial Chemical Industries Ltd.

The problems of the dyestuff factory fall into four main groups, so that there is a corresponding number of chemical sections; the Research and the Dyehouse Departments are responsible for development work, whereas the Analytical and the Manufacturing Departments are concerned mainly with the efficient carrying out of the processes already in operation for the manufacture of intermediates for dyestuffs and the dyestuffs themselves.

The work of the Research Department at Blackley can be considered under three broad headings: the first is the improvement of existing processes by increasing the yields of dyestuff or other material being made, by simplifying the methods of manufacture, by improving the quality, such as shade and appearance of dyes, and by any other means that may seem possible. This section of the Research Department maintains close contact with the manufacturing works, because its investigations have a direct influence on the processes carried out in the factory. The second aspect of the research work is mainly concerned with the products of other dyestuff manufacturers in England and abroad: in order to maintain its position it is evident that a modern industry must be fully cognisant of the products of its competitors, and in the research laboratory some of these are examined and their constitution determined. Further action may be taken if it is permissible or considered desirable. Under the third heading comes what may be termed exploratory work, the object of which is to try to invent new dyestuffs having specially

desirable properties, and to find how they may be manufactured in an economical manner. In conjunction with the Research Department there is an experimental works-plant where new processes, after having proved to be successful in the laboratory, can be tried out on a larger scale, comparable with that used in the manufacturing works, and improvements made before they are actually employed for factory production.

The personnel of the research laboratory is divided into a number of sections, the members of each section restricting themselves, as far as possible, to their own specialised, or closely allied, problems. The main divisions, which indicate the scope of the investigations carried out, are Azo Dyestuffs, Lake Mordant Colours, Vat Dyestuffs, Basic Dyestuffs, Intermediates, Rubber Chemicals, Synthetic Resins, Biological Chemicals, and Auxiliary Textile Chemicals. In addition a Physical Chemistry section is responsible for work on the physical condition of powders, pastes and emulsions, for microscopic investigations, and for experiments involving electrical measurements; and the Analytical section carries out research on new analytical methods, on the means of identifying various substances, and on micro-analysis, that is analysis using minute amounts of materials.

Associated with, and in fact indispensable to, the work of the Research Department is the library and information section; here are to be found the current and back numbers of some two hundred technical journals in English, French, and German, as well as details of a large number of British and foreign patent specifications. A considerable number of reference books are available in the library, and there are also facilities for obtaining almost any book that may be required from outside sources. The library acts as the intelligence department of the firm: all technical records are kept there, and from it there are issued weekly and monthly bulletins giving scientific and technical information of various kinds, consisting of abstracts of published papers and reports of work carried out in the firm's laboratories and works. In this way the research chemists are kept abreast of all discoveries which are likely to be of importance to them in their investigations; not only is valuable time saved but information which might otherwise have been overlooked is made readily available. Translation of articles in foreign technical journals is also carried out as one of the library activities.

The second main development section of the laboratory organisation of the dyestuff factory is to be found in the Dyehouse Department, the work of which falls into two chief groups, according as to whether the particular investigation is for the direct benefit of the Dyestuffs Group of Imperial Chemical Industries Ltd., or for the benefit of its customers. The latter aspect provides the main bulk of the work of the Dyehouse Department, and so it may be regarded essentially as a technical service section. The work done for the firm itself deals with the examination of the tinctorial properties and the fastness to light, washing, ironing, perspiration and to various textile manufacturing processes, of new dyestuffs made in the Research Department and of products marketed by competitors; comparisons are also made of the quality of current products of the firm and similar products of other firms. Research into new applications of dyestuffs and other substances is also carried out in the Dyehouse Department. This department is responsible for the production of pattern cards showing the many dyes made by Imperial Chemical Industries Ltd., and for the preparation of technical literature.

The work for customers is concerned chiefly with recommending appropriate colouring matters for particular purposes, with the investigation of faults encountered in the use of dyestuffs in various industries, and with the giving of advice concerning the lay-out of plant and the processes to be used in new dye-using factories. In the execution of duties of this nature members of the technical staff of the Blackley dyestuffs laboratories are constantly visiting the works of customers; during 1934 about two thousand such visits were made. The problems of the Dyehouse Department are concerned with the following industries, in all of which dyestuffs or pigments are used: leather manufacture and dyeing, paper manufacture, paint and printing-ink making, the rubber trade, the various sections of the textile industry, e.g., cotton, wool, silk and artificial silk dyeing and calico printing, the dyeing of furs and feathers, and the colouring of food materials. The technical staff of the department includes persons who are experts in, and have had practical experience of, the various industries enumerated: many of them have in addition high scientific qualifications, so that they are eminently fitted to act as intermediaries between the dyestuffs manufacturer and the user.



FIG. 19.—LEATHER DYEING LABORATORY
(By courtesy of British Dyestuffs Corporation, Ltd.)



FIG. 50. TENTH PRINTING LABORATORY

Many of the problems set the Dyehouse Department are unique and so the experimental apparatus has to be extemporised for each investigation ; there is, however, a considerable amount of permanent equipment of the type actually employed in the dye-using industries. The calico-printing section, for example, possesses several printing machines, the leather section is equipped with drums, paddles, glazing-jack, and other apparatus peculiar to the industry, and in the rubber department are to be found presses, autoclaves, mills, etc., such as are normally employed in the manufacture of rubber goods. Various devices are also used for carrying out accelerated ageing tests on dyed materials, weathering tests on varnish films, and for determining the drying time of the synthetic resin basis of quick-drying paints.

There still remain the Analytical and Manufacturing Departments to which brief reference must be made. In the analytical section the examination of all raw materials and intermediate products used in the manufacture of dyes is carried out ; special search is made for the presence of impurities likely to have a deleterious effect. The finished dyestuffs are also submitted to the Analytical Department for chemical examination, although the tinctorial properties are studied by the Manufacturing Department. Besides the study of new analytical methods and the preparation of the special solutions required in the laboratory, a careful control is kept on all waste products, such as water effluents and flue-gases leaving the factory ; in this way leakage of valuable material and the inefficient working of the boilers can be detected, and possible nuisances can be avoided.

The work of the laboratories of the Manufacturing Department is divided into two sections ; the first deals with the intermediate stages of dyestuff manufacture and carries out the chemical control tests necessary to follow the progress of the operations, whereas the work of the second is tinctorial rather than chemical, that is to say, actual dyeing tests on fabrics largely replace ordinary chemical analysis. After the intermediates have been passed as satisfactory from the analytical viewpoint, they are used for making test quantities of dyes in the laboratory and their dyeing qualities examined ; similar tests are applied during the stages of manufacture and also on the finished product. Any harmful factor not made evident by chemical analysis is brought to light in this manner, and careful control at every point, both chemical and tinctorial, is not only to the advantage

of the manufacturer, it also ensures that the user of dyestuffs is supplied with reliable products.

THE LABORATORIES OF THE BOOTS PURE DRUG CO. LTD.

In the manufacture of fine chemicals, mainly for medicinal and toilet purposes, it is evident that careful analytical control both of the raw materials and the final products, as well as of the intermediate stages of manufacture, is essential. The presence of deleterious impurities in fine chemicals may do infinite harm, both to the user and the maker, and so it is not surprising that in the largest pharmaceutical factory in Great Britain, namely, the one recently erected for the Boots Pure Drug Co. Ltd., at Beeston, Notts, the analytical laboratory should be such an important feature. This laboratory, having a floor-space of over 17,000 square feet, occupies the whole frontage of the building shown in Fig. 21 at the second and third floor levels; the upper floor is cut away so as to leave extensive wells, surrounded by balconies, providing about 18 feet of head room above the working benches (see Fig. 22). With such spacious accommodation, giving plenty of light and air, the chemical work can be carried out under the best possible conditions.

The offices and libraries are situated at the centre of the laboratory, and a gangway eight feet wide runs the whole length, with working benches on either side; special benches for balances, burettes, fume-chambers and muffle-furnaces are placed at convenient intervals throughout the laboratory. The main fume-chambers are built in combination with the chambers for muffle-furnaces, gas ovens, etc., as may be seen in the photograph; this ingenious arrangement permits the use of the upward draught, caused by the rising hot air from the furnaces, to ventilate the fume-chambers. All the fumes, both from the chambers and the gas-furnaces, are carried off through a vertical chimney passing through the roof.

Service pipes conveying water, gas, electric-power lines, compressed air and vacuum are carried in a special trench running almost entirely around the laboratory, with branches to each bench; drainage from all sinks and working benches runs into surface drains passing under the ends of the benches on either side of the central gangway. The trenches for service pipes and drains are covered with tarred wood, faced with linoleum, flush

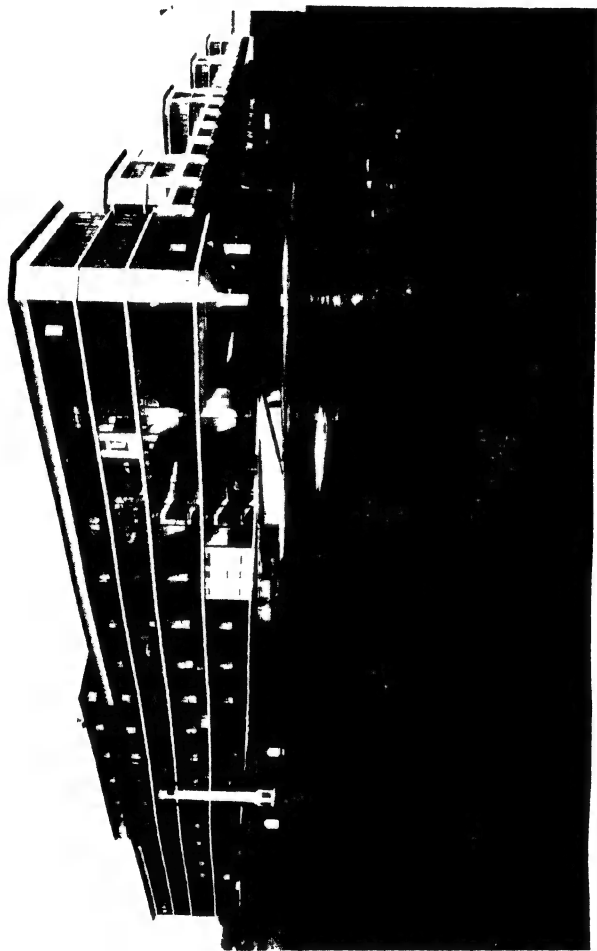


FIG 21 —BOOTS PURE DRUG CO LTD , BEESTON FACTORY
(The Analytical Laboratories occupy the front of the building at second and third floor levels)



FIG. 22.—ROOTS PURE DRUG CO. LTD., ANALYTICAL LABORATORY

with the rest of the floor ; the covers are screwed down in sections for convenience of inspection and cleaning. These features may be clearly observed in the photograph in Fig. 22.

For convenience in dealing with the many problems associated with the manufacture of toilet and pharmaceutical products the work of the analytical department is divided into seven main sections, each in charge of a superintendent chemist. A brief account of the work of these sections will indicate the variety and scope of the duties falling to a chemist to carry out ; it will also show the importance of chemistry in manufacturing processes.

The first section is responsible for the routine examination of all raw materials, such as vegetable products from which drugs are extracted ; this department also carries out any microscopical work required in other parts of the laboratory. In a second section the finished pharmaceutical products are examined, whilst a third is responsible for all toilet preparations immediately prior to sale. A fourth section carries out the examination of all drugs and fine chemicals, either in the finished state or for use in further manufacture, purchased from outside firms. Investigation work of a non-routine character, such as various matters arising out of manufacture and sale, and the handling of complaints, is carried out by a fifth department ; this section also deals with the development of new products and the modification of formulæ for the improvement of products already being made. After work of this type has been carried as far as possible in the analytical laboratory, it is passed on to a special laboratory in the works, where experimental batches of the new material or the new processes can be tried out on a small plant scale. The sixth division of the laboratory deals with the inspection of containers, packing material and printed matter used in the packing departments ; this section is regarded as being possibly unique in the pharmaceutical and perfumery industries : it ensures that the products of the factory are enclosed in well-made bottles and jars, or in durable tubes made from suitable metals.

The last section of the analytical department is separate from the laboratory already described ; it is one which it is at first sight surprising to find associated with a pharmaceutical factory : a little further consideration shows, however, that it represents an enlightened manufacturer's realisation of the importance of scientific control at every stage. A specialised laboratory unit

is devoted to the study of chemical engineering and related problems : this consists mainly of a metallographic and mechanical testing laboratory and a chemical laboratory for the investigation of metals and alloys, and chemical problems of an engineering nature. The chemical laboratory has an electric tube-furnace for the determination of carbon in steel, an electric muffle-furnace, and corrosion-testing apparatus. In this section constructional materials are given a thorough test before being adopted in the manufacturing plant.

In the manufacture of pharmaceutical and toilet products on a large scale every precaution must be taken to avoid even minute contamination by metals. The special laboratory carries out investigations into the best metals or alloys to be used for the construction of large vessels, such as storage tanks, jacketed steam pans, etc. Quite apart from the danger of contamination there is also the desire to avoid corrosion and the phenomenon known as " weld decay " in order to prolong the life of the vessels. It is of interest to note that as a result of the work carried out in this laboratory special stainless steels, containing small amounts of tungsten and titanium, were used in the Beeston factory ; this was the first time such steels were employed on a large scale.

The Analytical Department employs a total staff of nearly eighty, including fully qualified chemists, metallurgists, and pharmacists, and other skilled and semi-skilled assistants.

In addition to the sections already described the Boots Pure Drug Co. Ltd. has a separate department devoted entirely to research ; this department was started in 1915 in order to develop processes for the manufacture of various synthetic products and fine chemicals which had previously been obtained from abroad. In 1921, on the appointment of Dr. F. L. Pyman, F.R.S., as Director of Research, the laboratories were considerably enlarged and the personnel increased ; at the same time their scope was widened by the inclusion of the Pharmacological and Bacteriological Departments. The new chemical research laboratory covers a floor space of about 12,000 square feet, and includes provision for the offices of the Director, with a private laboratory for his use, together with a library well provided with current scientific journals and books. The work carried on in the Research Department includes investigations into the processes for making fine chemicals with the object either of finding new methods or of

improving those already in use. Fundamental researches in chemotherapy and the relation between chemical constitution and physiological action are also undertaken in this department.

IV.—THE CHEMICAL RESEARCH LABORATORY, TEDDINGTON

As an example of an establishment under the Department of Scientific and Industrial Research, which is devoted exclusively to research work, may be taken the Chemical Research Laboratory at Teddington, Middlesex. The following description is taken from the address by Professor G. T. Morgan, the Director of the Laboratory, to Section B (Chemistry) of the British Association for the Advancement of Science, at Bristol on September 4th, 1930. "The Department had at various times become interested in investigations of a chemical nature, such, for example, as (1) large-scale researches on the chlorination of methane; (2) large-scale researches on the production of formaldehyde; (3) investigations on the production of glycerine; (4) investigations on the manufacture of products from fish residues; (5) general researches on the corrosion of metals; (6) general researches on high-pressure reactions, including the reactions between carbon monoxide and hydrogen.

"These investigations, which were undertaken mainly under the auspices of the Chemistry Co-ordinating Research Board, were carried out by isolated groups of workers, who were often located in widely separated laboratories. One group studied the corrosion of metals at the Royal School of Mines, another examined fish products in the Imperial College of Science and Technology, whereas a third experimented on the chlorination of methane and on the recovery of formaldehyde from waste liquors of wool-scouring at the Royal Naval Cordite Factory in Dorsetshire.

"It soon became evident that some increase in economy and efficiency could be attained by bringing together under one roof these scattered groups of workers who would receive encouragement and stimulus by becoming part of a more centralised scientific organisation. A suitable site was chosen on the Bushy Park Estate in close proximity to the National Physical Laboratory and the Admiralty Research Laboratory, and here in 1924 the building of a chemical laboratory was commenced on a plot of land allowing ample scope for future expansion.

“The original plans drawn out by the architects of H.M. Office of Works made provision for three laboratory units each of rectangular shape and built round four sides of a central courtyard. The front and back of the hollow rectangle consist of two two-storey blocks; the front block designed for general and special small-scale laboratories with the necessary offices, the back block arranged to accommodate workshops, service rooms, and heating plant. The two sides of the rectangle, which consist of two single-storey blocks with saw-toothed roofs, north lighted and with a clear head room of about 16 feet, give adequate space for large-scale chemical plant.

“These buildings are constructed in steel and brick and so arranged that partitions can be readily removed for alterations or extensions. In the two-storey blocks the floors and roofs are formed of hollow concrete tubes, but in the engineering section of the building, where heavy superloading had to be considered, a more rigid type of construction in steel and concrete floors was adopted. In the interest of economy, plaster and other relatively expensive internal finishings were omitted wherever possible, any distemper or paint being applied to flush-pointed brickwork. The floors were covered with stout cork carpet, laid directly on the cement rendering.

“The laboratories are equipped with specially designed fittings, the framing and fronts are of stained British Columbia pine, whereas the bench tops and other portions subjected to hard wear are in teak or Iroko wood. The internal drainage to laboratory sinks is effected by open stone-ware, three-quarter circular channels finished with acid-resisting glaze. Wherever exposed internally, structural steel and joiners' work are coated with acid-resisting paint. The benches of small-scale and special laboratories carry five services—gas, water, steam, vacuum, and compressed air. Each room is amply supplied with electric current (D.C.).

“In conformity with the neighbouring buildings of the National Physical Laboratory, a simple modern Georgian style was adopted in the design of the elevations of the new laboratory. The buildings are faced externally with multi-stone sand face bricks, reconstructed Portland stone being used sparingly in cornices, string courses, and entrance doorways.

“The construction of one of these units was started towards the end of 1924, and when scientific work was commenced in the

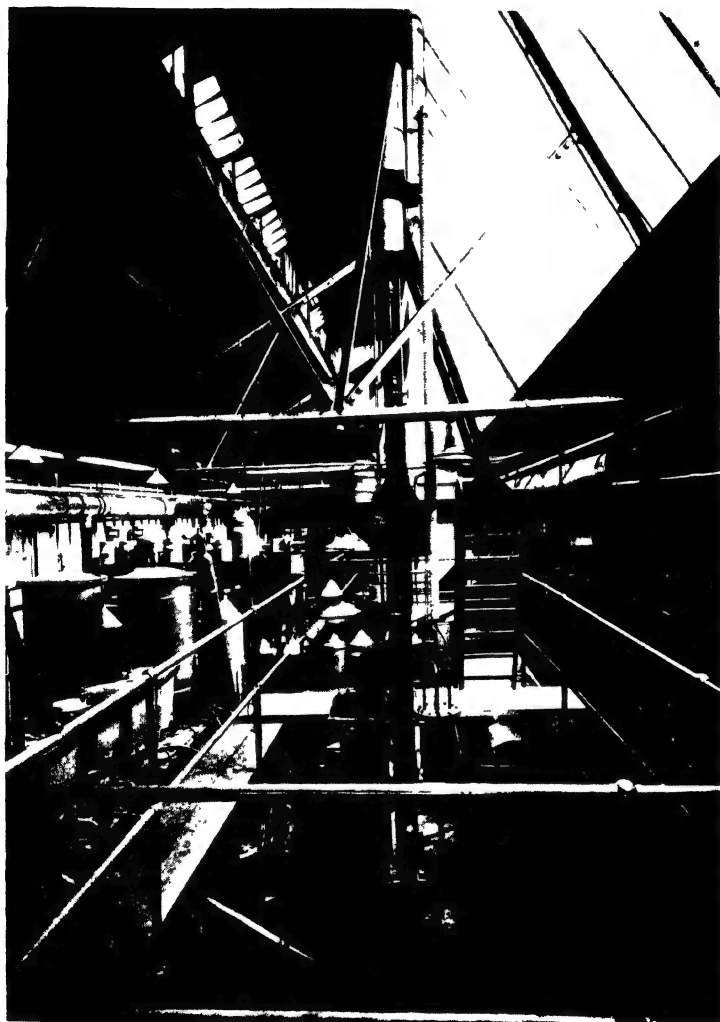


FIG 23.—CHEMICAL RESEARCH LABORATORY (DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH), TEDDINGTON SOLVENT EXTRACTOR FOR LOW-TEMPERATURE TAR RESEARCH

(Crown Copyright Reserved)

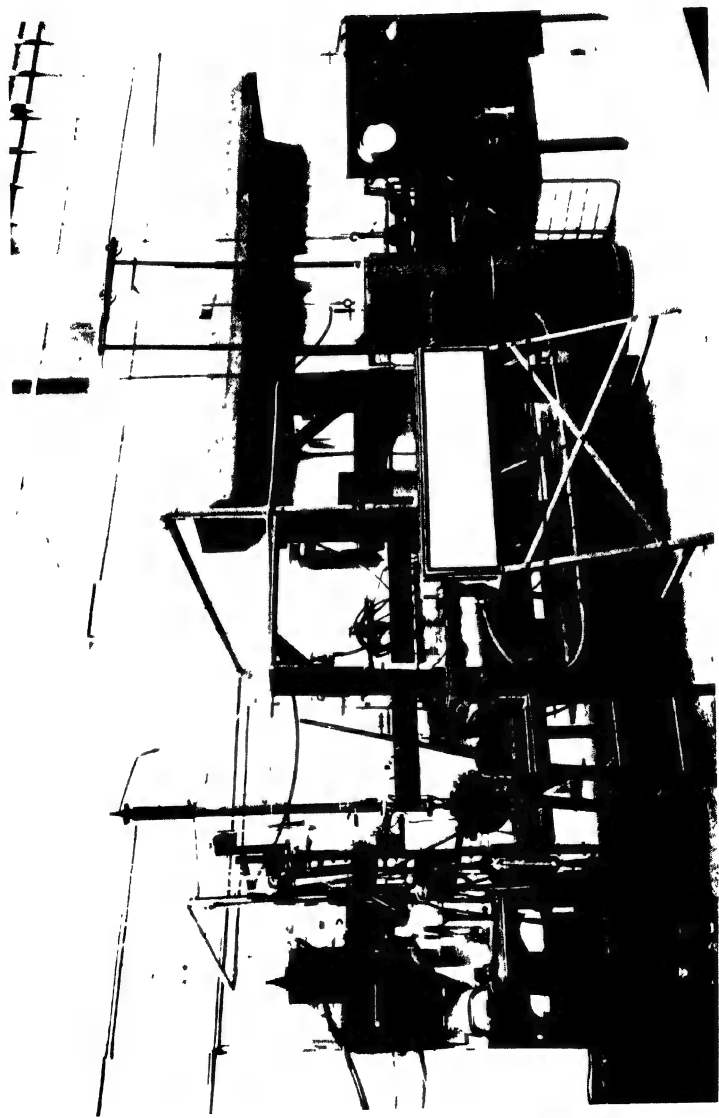


FIG 24 —CHEMICAL RESEARCH LABORATORY, TEDDINGTON HELIUM PLANT
(Crown Copyright Reserved)

autumn of 1925 about one-third of the first unit had been built, although actually only one room was ready for occupation. The fitting of the remaining laboratories and workshops was, however, rapidly effected and by the end of 1926 the whole of the available space was fully occupied, the staff then consisting of the superintendent and ten chemists, with one engineering assistant and ten members of the artisan, clerical and general staff.

"The frontage to the half unit was commenced in November, 1927, and completed for occupation by Easter, 1928, and the staff was then increased gradually to its present total strength of about sixty.

"Beyond a small addition for stores and workrooms, completed in 1929, there has been no further extension of the building, so that after five years rather more than half of the first unit has been erected and put into commission. There has been no attempt to force the growth of this State laboratory, which is still to be regarded as being in the experimental stage.

"The work of the laboratory is conducted under the guidance of a Chemistry Research Board, which has taken over certain functions of the older Chemistry Co-ordinating Board. This Board is charged with the duty of advising the Department (of Scientific and Industrial Research) on the programme of work to be undertaken at the laboratory and of exercising general supervision over its execution. . . . Executive control . . . has been vested in a whole-time Director.

"At the present time the scientific and technical staffs are occupied on six specific items of research prescribed on the advice of the Chemistry Research Board, and 'working parties of exploration' are detailed to these researches by the Director. When thus arranged (in chronological order), the six mandated researches are as follows: synthetic resins, low-temperature tar, high-pressure chemistry, corrosion of metals, chemotherapy, and research on water pollution. In addition to these prescribed investigations, a certain amount of general research (of an academic character) is carried out at the discretion of the Director."

Since this account was written in 1930 the first unit of three contemplated has been completed, so that the accommodation has been almost doubled; the total staff is now seventy-five, including four workers from other organisations who are studying methods in use at the Research Laboratory. In addition to the

researches already mentioned, studies are being undertaken of road tars, of the substances used in artificial dentures, and of various chemical engineering problems, particularly those connected with work at very high pressures. A full account of the work of the Laboratory up to the end of 1934 is given in the Report of the Chemistry Research Board recently published by H.M. Stationery Office.

SHIRLEY INSTITUTE—THE BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION

The Research Association of the Cotton Industry is an excellent example of an important post-war development in co-operative research, and it would be of interest to give a short account of the origin and work of this Association. Although its activities are by no means entirely chemical, this aspect is evidently regarded as important since eminent chemists, the late Dr. A. W. Crossley, F.R.S., and Dr. R. H. Pickard, F.R.S., were chosen as the first two Directors of Research. As already indicated previously a number of other industries have formed research associations along similar lines to the one now to be described.

In January, 1916, the Department of Scientific and Industrial Research approached certain prominent cotton manufacturers with the object of ascertaining whether it was desirable or necessary to encourage research in the cotton industry: it was generally agreed that the success of this industry, like that of others, is dependent on cheaper and better methods of production, and that only by carefully planned, systematic and continued application of science to the principles and practice of the industry could its economic position be maintained. It could hardly be expected that individual firms could undertake such a task, and so, under the stimulus of the Advisory Committee of the Scientific and Industrial Research Department, a Cotton Industry Research Association was formed with the object of carrying out co-operative research into the problems of the industry. The funds of the Association are at the present time derived from contributions from about 1200 firms, together with grants from the Government and from the Cotton Trade War Memorial Fund.

Past experience had revealed the disadvantage of investigations



FIG 25 —CHEMICAL RESEARCH LABORATORY (DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH)
TEDDINGTON

(*Crown Copyright Reserved*)



FIG 20—SHIRLEY INSTITUTE, MANCHESTER, 1930 COTTON RESEARCH LABORATORIES AND WORKSHOPS
(Further considerable extensions are in progress in 1935)

from the point of view of any one branch of science such many-sided problems as are presented for solution by the cotton industry. It was felt that the desired results could only be forthcoming when the chemist, the colloid chemist, the physicist, the botanist, the technologist and perhaps also the engineer were brought together under one roof, not as individuals, each searching for a solution of some definite problem in his own science, but as a body of workers co-operating under the guidance of one director.

To carry out this objective a house and an estate of about $14\frac{1}{2}$ acres, at Didsbury, Manchester, were acquired in 1920, and plans were developed for the formation of a research organisation, now called the Shirley Institute, providing for a library and information bureau, administrative offices, laboratories, and workshops. The library and offices were found accommodation in the already existing house, whereas special buildings were erected for the other activities. The new building originally covered an area of some 12,000 square feet: this was doubled by 1930, and is now undergoing further considerable extension. It is of one storey, raised four feet above the ground level, with outer walls 21 inches thick, and having a saw-toothed roof to provide for north-lighting. A "unit-size" room was designed, 22 feet by 10 feet 6 inches, and the actual laboratories were made multiples of this unit; the dividing walls are of breeze-block, plastered over, and are independent of the roof load, so that they can be easily removed if it is desired to increase or diminish the size of any room. The actual fitments of each laboratory depend on the purpose for which it is being employed; the equipment is designed to be as mobile as possible, so that interchanges and alterations can be readily made.

The work of the Institute was at first divided into sections, e.g. chemical, physical, botanical, etc., determined by purely scientific considerations, but this has now been changed and the activities are divided according to the main problems of the cotton industry: these are spinning, sizing, weaving, bleaching, dyeing, testing, and rayon (artificial silk), and in addition there are sections dealing with mycology and statistics. The library and information bureau represents an important activity of the Shirley Institute, and three graduates, in addition to other assistants, are fully occupied in this aspect of the work. The total staff is over two hundred, of whom some seventy are

University graduates in one or other branch of science or technology.

It would be out of place to attempt to give here an account of all the multifarious activities of the Shirley Institute and of their relationship to the cotton industry ; apart from indications of the chemical problems, given below, it will perhaps be sufficient to state that in addition to the fundamental research work being regularly carried out with the object of improving methods and increasing the efficiency of the cotton trade over a thousand enquiries are received annually from spinners, manufacturers, dyers, and others. Among the problems having chemical interest which have been and are being studied in the Cotton Research Association laboratories are the identification by chemical means of cottons from different sources ; the " sizing " of cotton yarns ; scouring and bleaching ; removal of oil stains from cloth before bleaching ; removal of rust stains ; and dyeing and printing of fabrics. It is interesting to record that as a result of the work on the removal of oil stains, a specific soap, known as Shirley soap, made from coconut-oil, was invented which has been found to be very effective.

Since the opening of the Institute about 180 papers reporting the results of work carried out there have been published in the *Journal of the Textile Institute*, in addition to many reports circulated privately amongst the firms belonging to the Association. There is little doubt that the cotton industry has already benefited considerably from the research work of the Shirley Institute, as is witnessed by the fact that financial support is still forthcoming in spite of the recent depressed state of the trade in Lancashire.

CHAPTER III

APPARATUS

ON entering a chemical laboratory the first impression on the mind of a visitor not conversant with the science of chemistry and its practice is produced by the apparently innumerable ranks of bottles. This is particularly noticeable in those laboratories in which provision is made for a large number of students,

inasmuch as each worker requires for his individual use a considerable number (about thirty) of "reagents," liquid or solid, which are so frequently in use that it would be a source of great inconvenience if they were shared with a neighbour. Beside these there are usually stacks of shelves placed in a position of easy access, so that the bottles of solutions or other materials which are in less frequent demand may be ready for common use by any of the occupants of the laboratory.

Laboratories which are devoted to other purposes than the teaching of bodies of students do not generally display so prominently any large array of bottles. By reference to some of the illustrations which show the interior of laboratories employed for special purposes it will be seen that bottles do not always form a conspicuous feature. In such cases apparatus connected with the special business of the laboratory will catch the eye. It may be apparatus for distillation, for the estimation of melting points or freezing points, for electrolytic or other electrical operations, and so forth; in any case glass vessels of all shapes and sizes, glass tubes contorted into a variety of forms, and the appearance of the Bunsen blue cone of burning gas at many places will be prominent features of the chemical laboratory.

Detailed descriptions of apparatus would alone occupy a large volume, and since the purpose of this book is general, no attempt will be made to describe apparatus which has long been a familiar part of the indispensable equipment.

Weighing.—Every chemist must possess at least one balance of precision which will carry 100 to 200 grams in each scale and turn with a difference of $\frac{1}{10}$ th milligram. With the same instrument, however, and a smaller mass in the pan, and using the method of vibrations, much smaller differences can be recognised. The chief change in the construction of chemical balances which has become general within the last thirty years is the shortening of the beam, in consequence of which its oscillations are quicker, and therefore the business of weighing is abbreviated.

The ordinary balance agrees in principle with the common systems of scales and weights, and differs from the pillar scales of the grocer or druggist only in superiority of workmanship and materials whereby it is made vastly more accurate and sensitive. The accompanying illustration shows an ordinary

short beam balance of modern type. It consists of a two-armed lever, the centre point of which is suspended on a knife edge which rests on a plane surface of agate. The pans are also suspended on knife edges resting on agate planes when the balance is in use. When not actually in operation the beam and the pan supports are raised from contact with the planes. This is accomplished by turning the screw head in the middle

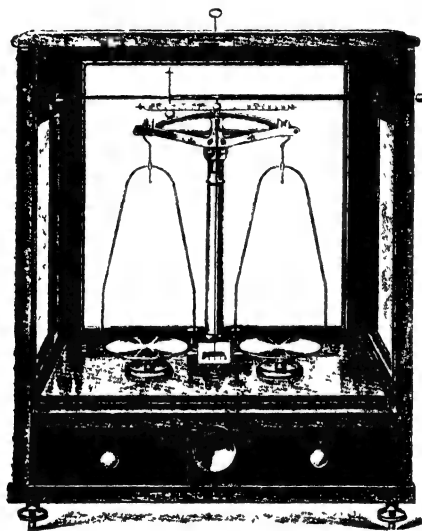


FIG. 27. A SHORT BEAM BALANCE

of the box below. The divided scale above the beam carries a small rider of wire, the position of which can be altered, and the final adjustment of weight effected.

For assay work with precious metals, when small quantities only are being weighed, special balances are generally used: these usually have quite short beams and the moving parts are made as light as possible consistent with strength. They can only be used with weights of less than 20 grams, and

are then sensitive to changes of $\frac{1}{1000}$ th part of a milligram. This type of balance has been further improved in recent years because of the growing popularity of micro-chemical analysis, that is, analysis with only small quantities of material, and by using specially ground knife edges a sensitivity of $\frac{1}{1000}$ th milligram is attainable. It is hardly necessary to mention that great care is required in its operation.

The balance about to be described differs in principle from all ordinary balances, and in the skilled hands of the inventors and others exhibits a degree of sensitiveness and delicacy in dealing with small masses which has hitherto been unheard of. It is obviously applicable only to exceptional cases.

The new balance is described by the inventors, Professor



*Yours sincerely,
William Ramsay*

B. D. Steele and Mr. Kerr Grant, in the Proceedings of the Royal Society for 1909, and in addition to the interest attaching to the application of the fundamental idea involved, a balance of this construction with some modifications in detail was used by Sir William Ramsay¹ and Professor R. Whytlaw-Gray in determining the density of the gaseous emanation from radium (q.v.) which Ramsay called "niton." A similar principle has been used quite recently by Professor Whytlaw-Gray and his collaborators, in the University of Leeds, for the accurate determination of the densities of gases, with the object of finding the atomic weights of various elements.

The rationale of the method of weighing is as follows: If a bulb filled with air is at the same temperature and pressure as the air surrounding it the *net* weight of the contained air will be nothing. This is in accordance with the principle of Archimedes. If, however, the pressure of the air surrounding the bulb is altered, the sealed up air exerts more or less of its full weight. By suspending a bulb containing a known quantity of air at one arm of a balance, and arranging the whole instrument within a case from which the air can be pumped out to any desired extent, the effective weight of the bulb of air can be changed to any amount desired.

Temperature changes are eliminated as far as possible, as well as vibration, by mounting the balance on a stone pillar in a cellar, and placing the brass case of the balance inside a large box of bright tin plate. The diagram in Fig. 28 will give an idea of the essential parts of the micro-balance of Steele and Grant.

¹ William Ramsay, born at Glasgow on October 2nd, 1852, was the son of a civil engineer; he attended Glasgow Academy, and the universities of Glasgow, Heidelberg and Tübingen. He occupied successively the positions of Assistant at the Glasgow Technical College (1872), Glasgow University (1874), Professor of Chemistry at University College, Bristol (1880), where he became Principal in 1881, and finally Professor at University College, London (1887), from which post he retired in 1913. Ramsay's name will, of course, always be associated with the discovery of the inert gases of the atmosphere, described later in the text; in recognition of the importance and interest of this discovery, and the skill displayed, he was elected an honorary member of nearly every scientific academy in the world; he has also occupied high positions of honour in British scientific societies. Ramsay was elected a Fellow of the Royal Society in 1888, and received its Davy Medal in 1895; he was awarded the Longstaff Medal of the Chemical Society in 1897. In 1902 he was made a K.C.B., and in 1904 he received the Nobel Prize for Chemistry. Ramsay had very exceptional skill as a manipulator of apparatus, and was an excellent linguist; on occasions he addressed meetings in French, German and Italian, as well as in English. He died, after a painful illness, on July 23rd, 1916. In addition to his scientific writings and a number of text-books Ramsay published *Essays Biographical and Chemical*, which made most attractive reading.

A is the beam of the balance constructed in the form of two triangles base to base, and made of fused quartz rod, 0.6 millimetre in diameter; the whole weighing less than half a gram. The frame thus formed oscillates about a central knife edge, ground at the end of the vertical rod, and resting on a plane quartz plate *f*. Attached to this beam at its centre (but not shown here) is a tiny mirror, taking the place of the pointer in an ordinary balance.

At one arm of the balance is a quartz counterpoise, while at

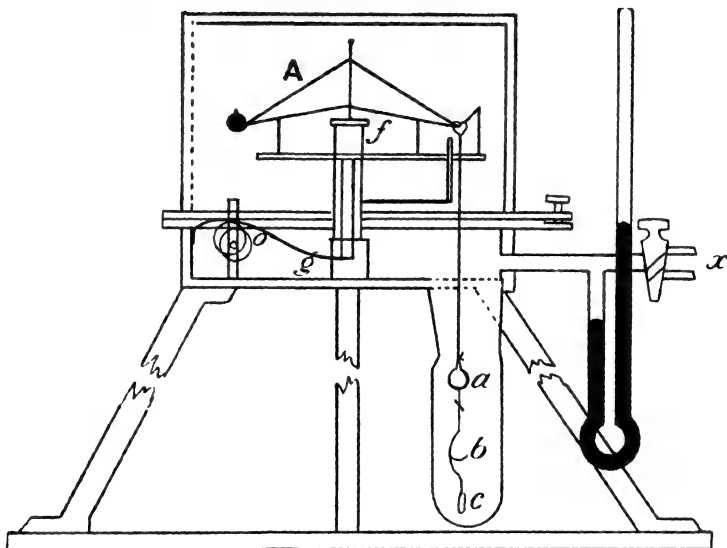


FIG. 28. MICRO-BALANCE OF STEELE AND GRANT

the opposite end is suspended a small quartz bulb of known internal volume, and sealed up at known temperature and pressure. This is hung by means of a fine quartz fibre within a tube which is connected air-tight to the bottom of the balance case. A fine hook carries the quartz bulb, *a*, and below this a quartz scale pan, *b*, and a quartz counterpoise, *c*. The weight of this suspended system is always adjusted to equilibrate the counterpoise attached to the opposite end of the balance.

The method of weighing is as follows: if the quantity of substance to be weighed does not exceed the total weight of the air contained in the bulb, the pressure inside the balance case

and the resting point having been taken with the scale pan empty, the substance to be weighed is placed on the pan and the pressure adjusted till the same resting point is obtained. If w is the total weight of air contained in the bulb, which was filled at pressure P , and P' represents the difference in pressure required to recover the original resting point, then the weight of the substance is wP'/P . If the quantity of substance to be weighed exceeds the weight of air contained in the bulb it is necessary to prepare one or more counterpoises which must be lighter than the original counterpoise c , and must differ from each other by a known amount not exceeding w .

The resting or zero point of the instrument is found by the position taken by the image of a Nernst lamp reflected from the mirror attached to the beam. The case is deprived of air by means of a vacuum pump connected through the two-way stop-cock x , and the pressure of the residual air is determined by observing the height of the mercury column in the manometer, which is read by means of a telescope and scale to a tenth of a millimetre.

The attachments for the release of the beam consist of two V-shaped quartz rods which just centre the beam but do not lift it. These can be lowered when required by means of the curved brass wire, g , connected as shown in the figure with the upright brass support. The wire is controlled by an excentric cam, o , rotated by a handle passing air-tight through a plug in the side of the case.

Such a description as the foregoing is only capable of giving an idea of the way in which the pneumatic principle is applied to the determination of weight. As to the possibilities of such a balance the statement of the authors is as follows: "Weights of the order of one-hundredth of a milligramme may be compared with the standard measures with an accuracy of one five-hundredth of their amounts, i.e. the absolute value of such weights can be determined with certainty to one fifty-thousandth of a milligramme (2×10^{-8} gramme), while changes of weight can be measured of an order as low as one two-hundred-and-fifty-thousandth of a milligramme."

With such appliances the mote in the sunbeam becomes a ponderable mass!

Heating and Cooling.—The common source of heat for the

purpose of ordinary experiment in the chemical laboratory is the combustion of coal-gas, generally in the Bunsen burner, or some modification of that familiar instrument in which the gas is mixed with sufficient air to secure complete and smokeless combustion.

As nearly everyone knows a much hotter flame is obtainable if the air is replaced by unmixed oxygen. The oxyhydrogen or oxy-coal-gas flame was at one time in common use for the production of the well-known limelight employed in the magic lantern and for theatrical purposes. Such a flame is also capable of piercing a sheet of iron, if not too thick, and may be used even for cutting armour plate.

The temperature of the oxyhydrogen flame is in the neighbourhood of 2000°C. , but a still hotter flame is produced when, in place of hydrogen, acetylene is used. The oxyacetylene flame may indeed be used for cutting armour plate six inches in thickness, at a rate more rapid than that of the saw. This, however, is not a laboratory operation.

The use of electric heating for warming houses and cooking has been introduced long ago, but the progress actually made was until recently comparatively slow. This method is based on the fact that when an electric current passes through an imperfect conductor more or less of the energy of the current appears as heat. An illustration of this is seen daily in the ordinary incandescent electric lamp, in which a thin wire of the metal tungsten is raised to such a temperature that a brilliant light results. The principle is applied in the heaters which for some purposes are used in the laboratory. Apparatus of this kind has several advantages: it provides a steady source of heat, spread over a larger surface than a flame, which may be increased at will from a gentle warmth to a low red if required, it is unaffected by draughts of air, and it is unattended by risk of fire when inflammable liquids, such as ether or alcohol, are to be heated. An example of the use of electric heaters is shown (Fig. 14, p. 35) in the distillation of wine, spirits, or beer, for the determination of their alcoholic strength. A measured quantity of the liquid to be tested is placed in the flask, distillation is continued till all the alcohol has passed over and a determinate quantity of liquid is collected. The specific gravity of this liquid, compared with the figures in an alcoholometric table, supplies the percentage of alcohol in the original liquid.

Another application to laboratory purposes is shown again (Fig. 16, p. 37) in the apparatus for steel analysis. The carbon left after dissolution of a weighed quantity of the metal in an appropriate solvent is burnt in a stream of oxygen in a tube heated by the current to redness. The resulting carbon dioxide is collected in weighed tubes containing caustic potash, as shown in the figure, and from the increase of weight the carbon in the sample can be calculated.

The use of the electric arc for the attainments of high temperatures is the result chiefly of the researches of the late Professor Henri Moissan,¹ whose untimely death in February, 1907, deprived the world of a very brilliant and indefatigable worker in science. One form of Moissan's furnace is shown in the adjoining illustration. The body of the furnace is formed of blocks of good lime, a material which resists without change the highest temperatures produced by the oxyhydrogen flame. In the arc lime slowly fuses and volatilises. As the diagram shows the carbon poles pass through the sides of the box and, being connected with the source of the current, are brought into contact with each other immediately over the object to be heated which is placed in the central cavity. On withdrawing the carbons apart, the arc is formed by the current carried across by a stream of carbon particles and vapour. The temperature produced in this way is higher than the temperature of any flame. It probably exceeds 3000° or 3500° C., but it is difficult to estimate. All ordinary metals not only melt in this furnace, but boil and pass off in vapour. Even lime and magnesia, among the most

¹ Moissan's career is both interesting and instructive. He was born in Paris September 28th, 1852, the son of an employé of the Eastern Railway Company, his mother assisting the slender resources of the family by working as a dress-maker. At the age of twelve he entered the municipal school at Meaux, where he remained till 1870. He then obtained a situation in a pharmacy, which he retained during two years, and then passed into Professor Dehérain's laboratory in the Museum of Natural History. Here he experienced the attractions of research, but, encouraged by Dehérain, he set to work privately to prepare for his degree, which he ultimately obtained. Subsequently he received an appointment at the *École Supérieure de Pharmacie*, where a few years later he succeeded to the chair of toxicology, and afterwards that of inorganic chemistry. At the time of his death he held the professorship of inorganic chemistry in the Faculty of Sciences of the University of Paris, where he had succeeded Troost in 1900.

To Moissan we owe the isolation (in 1886) of the elusive element fluorine, perhaps his most interesting work from the scientific point of view, and the discovery of the conditions of formation of the diamond. The latter discovery resulted from the experience he had gained in the application of the electric arc to the production of very high temperatures.

refractory oxides known, melt and ordinary charcoal is changed into graphite. In such a furnace Moissan saturated molten iron with carbon and cooled the mass rapidly, so as to produce solidification on the outside. The still fluid portion within had to cool under the great pressure which results from the tendency to expansion during the solidification of the iron. A small portion of the carbon crystallises under these circumstances in the form of the diamond. In order to separate these small

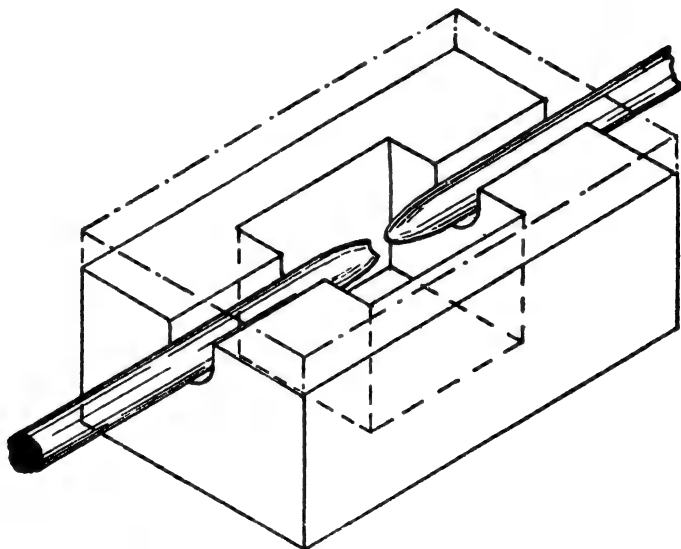


FIG. 29. MOISSAN'S ELECTRIC FURNACE

crystals the iron has to be dissolved away by means of acids, and the carbonaceous residue is again treated with an oxidising mixture of sulphuric acid and nitre to remove the graphite, while siliceous impurities are afterwards got rid of by use of hydrofluoric acid. In the end the small grains which remain are examined under the microscope. The largest diamond obtained by this process only measured half a millimetre in diameter, but Moissan proved the identity of these tiny crystals with natural diamond not only by reference to their crystalline form, but by their density (about 3.3 to 3.5), their hardness, being able to scratch ruby, and by their combustibility in oxygen.

Another product of the electric furnace is the substance

carborundum, a compound of carbon with the allied element silicon. This is produced by heating together fine sand (silica) with carbon and a little common salt. Carborundum has become very valuable, on account of its hardness, as a material for grinding and cutting metals in the engineering shop.

The most valuable of all products from the electric furnace is, however, calcium carbide. This again we owe to Moissan, who studied for the first time systematically the carbides of all the chief classes of metals.

The production of calcium carbide, CaC_2 , is simple enough. It results from the action of heat, in the electric furnace, on a mixture of ground lime and coke. The carbon divides itself between the oxygen of the lime and the calcium, so that carbon monoxide gas escapes, while the carbide remains at the end of the operation as a grey solid or sometimes in the form of black crystals.

For about forty years calcium carbide has been manufactured as a source of acetylene gas, which is now a familiar illuminant, and, as already mentioned, is employed in conjunction with oxygen for the production of a high temperature blow-pipe flame. This gas is also being used in an ingenious process for the manufacture of acetic acid, from which acetic anhydride and acetone can be obtained; all these products are required on a large scale in the new artificial silk and lacquer industries.

Acetylene is produced by allowing water to drip on the solid carbide placed in a suitable generator, and connected with a gas-holder in which the gas is collected over water.

Since 1903, however, calcium carbide has received application in a new direction, having been found to absorb nitrogen when heated to about 1000°C. , in the presence of small quantities of calcium chloride or some other salts. The product is the calcium salt of cyanamide, CN.NCa , and is known commercially as "nitrolime." It is a valuable nitrogenous manure (see p. 413).

The electric furnace is also used for the manufacture of graphite, a form of carbon, sometimes known in its natural form as *black lead* or *plumbago*; a mixture of powdered anthracite or coke and sand is placed in the furnace and strongly heated. The artificial product is said to be more expensive than naturally occurring graphite, but as it is softer it is used for lubricating purposes suspended in oil or water. The process is worked chiefly by the Acheson Company in the United States.

The application of the electric furnace to such operations as

the manufacture of steel is obviously a subject of the highest importance, but is outside the programme of the chemist.

The use of electrical methods for bringing about the combination of atmospheric nitrogen with oxygen, and the fixation of nitrogen and its oxides into solid compounds will be described in a later chapter.

Cooling.—Ice is an indispensable agent for use in the laboratory, especially in connection with the reactions in which carbon compounds are concerned. In very many cases the heat which is produced by chemical change goes on accumulating in the materials which have been mixed together until the temperature of the whole is such as either to cause the volatile ingredients to boil and evaporate away, or to give rise to new changes which may become violent and uncontrollable. The result is that the desired product is not secured and dangerous explosions may result.

The temperature of melting ice is always at 0°C. , but lower temperatures are easily obtained by mixing it with due proportions of very soluble salts. With common salt the temperature falls to the zero of the Fahrenheit scale ($-17^{\circ}\cdot 7\text{ C.}$), and a few pounds weight of such a mixture will keep a temperature of -12° to -15° for a long time.

Moissan in his experiments which resulted in the isolation of fluorine, made use of boiling methyl chloride as a frigorific agent maintaining a fairly steady temperature of -23°C. But much of the experiment during the last twenty years has required the employment of temperatures far below such limits, and even mixtures such as solid carbon dioxide in ether or alcohol, which gives a temperature of about -75°C. , are not low enough.

The liquefaction of atmospheric air in quantity has placed in the hands of the physicist and chemist an agent which has indirectly furnished the means of reducing the remaining more refractory gases, hydrogen and helium, to the liquid state. This achievement would, however, never have been reached but for the establishment of several important general principles which were only discovered in the course of nearly a century of laborious and sometimes dangerous experimental enquiry.

In all the older text-books of chemistry a distinction was made between the liquefiable or condensable gases and those which were called "permanent gases." No doubt the more

philosophical writers on the subject foresaw from the close resemblance between vapours and the more easily condensable gases, such as sulphur dioxide and chlorine, that after all there might be a similar relation between such gases and the so-called permanent ones, and it was expected that had suitable power been available the latter would prove to be also merely the vapours of very volatile liquids.

The difference between a vapour and a gas is now understood much more clearly, as will be explained presently.

The history of the liquefaction of all the gases need not be related in detail, but the following brief record will suffice to show the position of the question in the former half of the nineteenth century.

The list of gases below is accompanied by the names of the experimenters who succeeded in reducing them to the liquid state either by compression alone, or by compression assisted by the lowest temperatures then producible.

Name of Gas.	Observer.
Sulphurous acid (Sulphur dioxide).	Monge and Clouet, about 1880.
Sulphur dioxide and Chlorine.	Northmore, 1805.
Chlorine, hydrochloric acid, sulphur dioxide, sulphuretted hydrogen, carbon dioxide, nitrous oxide, cyanogen, ammonia.	} Faraday, before 1825.
Ethylene, hydrogen iodide, hydrogen bromide, phosphoretted hydrogen, silicon fluoride, boron fluoride, arsenetted hydrogen.	
Hydrogen, oxygen, nitrogen, nitric oxide, carbon monoxide, marsh gas.	} Faraday, before 1845.
	} Remained unliquefiable.

Experiments carried on by Thomas Andrews, Professor of Chemistry in Queen's College, Belfast, after several years of work gave the clue. In 1861 he described experiments in which he had submitted some of these remaining gases to very great pressures combined with cold, the pressure being limited by the capacity of the thick glass tubes to resist it. The cold was the temperature of the carbon dioxide and ether mixture which, under reduction of pressure, would go down to -160°F .

Atmospheric air was compressed to $\frac{1}{81\frac{1}{2}}$ th of its volume, in

which state its density was little inferior to that of water, oxygen to $\frac{1}{16}$ th, hydrogen to $\frac{1}{16}$ th, and so on, but in no case was there any appearance of liquefaction. But observations on the compression of carbon dioxide at different temperatures led to the discovery that when the gas contained in a tube is partly liquefied by pressure alone, on gradually raising the temperature to 31°C . (88°F .), "the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving

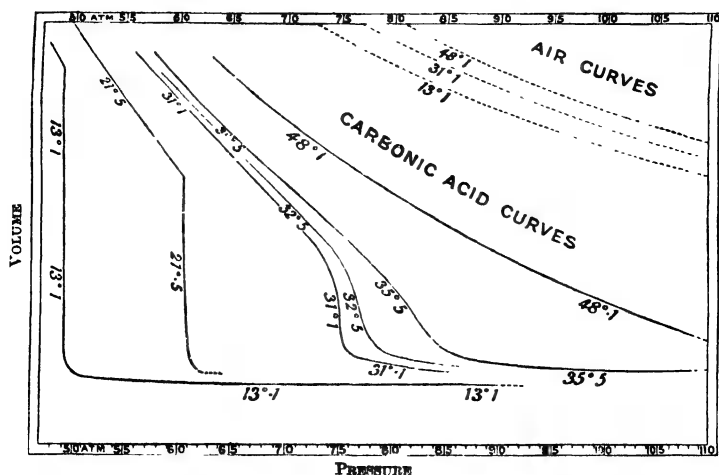


FIG. 30. CARBONIC ACID CURVES

or flickering striæ throughout its entire mass. At temperatures above 88°F . no apparent liquefaction of carbonic acid or separation into two distinct forms of matter could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."

A series of comparisons were then made by Dr. Andrews on the volume of carbon dioxide and air when submitted to increasing pressures at different degrees of temperature. When his results were plotted, the volumes against the pressures, a series of curves was obtained, in which it appears that air steadily diminishes in volume as pressure is applied at common temperatures, while carbon dioxide at temperatures considerably above

31° C. imitates it pretty closely. If the temperature, however, approaches within a few degrees of 31° a sudden diminution of volume is observed, which is indicated by a sudden change of direction of the curve, becoming vertical at anything below 31° with a pressure about 75 atmospheres (Fig. 30).

There is therefore a "critical point" of temperature above which carbon dioxide gas cannot be reduced to liquid by pressure. This has been shown to be true of all other gases, and the reason why oxygen, hydrogen, and some others had not been liquefied by pressure up to that time was that the temperature employed in each case had been above the critical point of the gas. The critical temperature for oxygen is about -118° C., while that of nitrogen is -146° C. Cooling the gas below these temperatures is therefore an essential condition for their liquefaction, and in the case of oxygen this result was attained, for the first time at the end of 1877 by the French physicist Cailletet and the Swiss professor Pictet, by two distinct methods.

But for the continuous production of the liquid from the gas yet another principle was necessary. Experiments made over eighty years ago by Dr. Joule of Manchester, in conjunction with William Thomson (afterwards Lord Kelvin), resulted in the discovery that if a gas is allowed to stream through a porous plug or an orifice cooling results. Joule and Thomson caused a stream of compressed gas to pass through a long copper spiral, immersed in water, at constant known temperature. The gas then escaped through the pores of a plug of compressed cotton wool, and its temperature was noted. In every case, except hydrogen, a reduction of temperature was observed which, though actually small in amount, was the greater the lower the temperature of the gas before passing through the plug. Thus the effect on carbon dioxide is shown in the following figures :

Temperature.		Degrees Cent.		
Before escape through plug	. .	12°·8	19°·1	91°·5
Reduction of temperature	. .	1·207	1·144	0·69

The amount of cooling is proportional to the difference of pressure before and after release, and inversely as the absolute temperature.¹

At low temperatures it has been found that hydrogen behaves

¹ The absolute temperature is obtained by adding 273° to the temperature in degrees Centigrade.

like other gases. These results afford information as to the internal constitution of gases, for in the experiments of Joule and Thomson the fall of temperature observed must be due to the performance of work in overcoming the mutual attractions of the gaseous molecules.

By compressing an ordinary gas, such as air, removing the heat produced by immersing the containing vessel in cold water or otherwise, and when cool allowing the gas to escape, a reduction of temperature is obtained. If this cold stream of escaping air is then made to pass over the pipe through which the gas passes previous to release, it may be cooled in a cumulative manner to lower and lower temperatures until it reaches a temperature below the critical point. By continuing the same process with comparatively moderate pressures a portion of the gas becomes liquid. This is the principle of the air liquefying plant to be found in the greater institutions for chemical and physical research.

Practical results on a large scale were first shown by Linde, an engineer of Munich, in 1895. Patents for the application of the same idea were taken out a little earlier in England by W. Hampson.

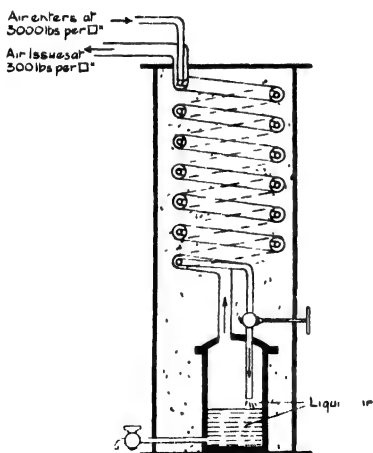


FIG. 31. CUMULATIVE COOLING
FOR LIQUEFACTION OF AIR

The apparatus actually employed consists of a compressor which, usually in two stages, puts the air, previously freed from water and carbon dioxide, under a pressure of 200 atmospheres. In this condition it is delivered into a close coil of copper tube, at the end of which is a small hole, the size of which can be regulated by a screw. Escaping from this orifice the cooled air returns to the atmosphere through a cylinder in which the copper pipe is coiled from which the air has just escaped, or through a

coil which encloses the return pipe as shown in the diagram. The cooling effect is thus economised on the regenerative system, just as heat is economised in a regenerative steel furnace. In

some machines the compressed air is cooled before escape by means of liquid carbon dioxide, but this is not necessary, as in a well-constructed machine liquid air begins to drip into the receiver soon after setting the pumps to work at atmospheric temperatures.

The liquid collected in this way has a very pale blue colour, and it boils at about -181°C . To attempt to collect it in any ordinary bottle would be like trying to catch water in a red-hot vessel. For when the liquid is poured into any vessel in the open air it boils furiously, and continues to do so till the two hundred degrees of difference of temperature has been abolished by the evaporation of a portion of the liquid. Even then heat reaches it from the outside far too rapidly to permit of keeping it for more than a very short time. To meet this difficulty Sir James Dewar's device of a vacuum jacketed glass vessel is everywhere adopted. The device is now familiar in the ordinary "Thermos" flask, which consists of two vessels, one inside the other, with a space between from which the air has been removed as completely as possible. A vessel of this kind is shown in section, page 77.

The vacuum vessel is rendered still more efficient by coating it with a thin but bright deposit of silver.

The low temperature of liquid air is demonstrable by many curious experiments. A tube full of mercury, which freezes at -39° , when plunged into liquid air, sets almost instantly to a solid resembling silver in appearance, and as malleable as lead. As is well known the mercurial thermometer is replaced in some latitudes, such as the north of Russia, by a thermometer containing absolute alcohol. This liquid dipped into liquid air at first assumes the consistency of oil, becoming more and more viscous till it sets into a glass-like solid. Such materials as fruit, flesh, and india-rubber cooled in liquid air become as brittle as glass, and when at this temperature they are struck with a hammer they fly to pieces.

The commercial production of liquid air has not only provided a valuable agent for the investigation of the properties of matter, but has led to some important practical results which will be described later on.

The history of the liquefaction of the gases would not be complete without reference to the two cases which have presented the greatest difficulty, namely, hydrogen and helium. The principles involved were perfectly well understood, the

difficulties arise in their application. First of all it is necessary to cool hydrogen gas to a temperature of about -80°C . before the evolution of heat observed in the Joule-Thomson experiments is changed into a cooling effect. Compression and release of hydrogen gas, therefore, bring the experimenter no nearer to the point of liquefaction unless the gas is already below that temperature. Then the critical point for hydrogen is at 238° to 240° below zero, or considerably more than 100° below the critical point of oxygen. There can be no liquefaction of hydrogen, therefore, no matter what pressure is employed, without the intense cooling obtained by causing liquid air to boil rapidly under reduced pressure. The self-intensive apparatus can then be used successfully. Liquid hydrogen is a colourless liquid with a well-defined surface, and having an extraordinarily low density. Bulk for bulk it has only about $\frac{1}{14}$ the weight of water. It boils at about -252° to -253°C ., and by rapid evaporation may be cooled till it sets into a wax-like mass resembling solid paraffin. The appearance of this solid at once dissipates the favourite theory advanced by Graham half a century or more ago, that hydrogen gas is the vapour of an extremely volatile metal. It certainly has many of the properties of a metal in the production of salts (acids), and in the readiness with which it exchanges places with metals in ordinary saline reactions. The significance of this exchange is, however, discounted by the fact that it also exchanges with chlorine and the other halogens which are at the opposite end of the electrochemical scale. Hydrogen gas is more nearly the analogue of marsh gas, CH_4 , and from one point of view may be regarded as the first term of the series of hydrocarbons called paraffins. Liquid hydrogen in quantity was first produced in an open vessel by Sir James Dewar in the laboratory of the Royal Institution in 1898.

One gas now remained, namely, the inert gas helium, which, discovered in 1895, was obtainable in moderate quantity. But it was another ten years before this exception to the rule, which could now be applied to gases generally, was abolished. Liquid hydrogen was now available as a cooling agent, and the liquefier being supplied with this powerful aid to condensation success was at last achieved.

To Professor H. Kamerlingh-Onnes, in the cryogenic laboratory directed for many years by him in the University of Leiden,

science owes this interesting result. More than 60 cubic centimetres (over 2 fluid ounces) of liquid helium were obtained, so that there could be no ambiguity about the result. In special laboratories where the properties of matter at extremely low temperatures are being studied, liquid helium is in use as a matter of course, much as liquid air was used thirty years ago. The boiling-point of liquid helium is estimated to be 268° to 269° below 0° C. The density of the liquid is 0.15, or less than $\frac{1}{6}$ the density of water, and a little more than twice the density of liquid hydrogen.

By causing liquid helium to boil under reduced pressure a temperature within 0.7° of the absolute zero, i.e. -273° C., has been attained, and even lower temperatures have been reached by methods, outside the scope of this book, in which liquid helium is employed.

At these very low temperatures the properties of many solid bodies are considerably modified. Thus the conductivity of metals diminishes with rise of temperature and increases with fall of temperature, and in the case of all the pure metals which have been examined the resistance at successively low temperatures down to about -200° is such that at the absolute zero it would disappear altogether. It

has been in fact observed that within 3° of the absolute zero many metals become such remarkably good conductors of electricity that they have been described as having "supraconductivity." The specific heats are also reduced as the temperature is diminished, and there seems evidence to show that they would all become zero at -273° C.; at temperatures in the region of 50° above the absolute zero the atomic heat,

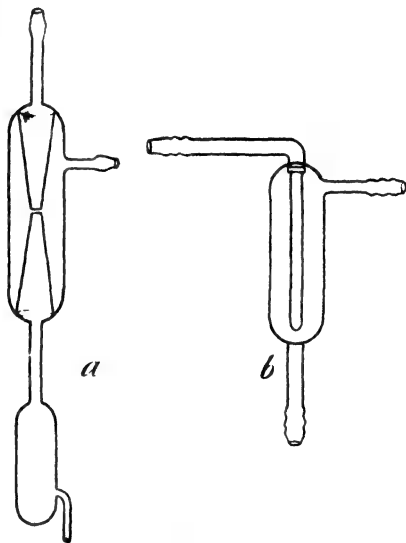


FIG. 32. FILTER-PUMPS

that is, the product of the specific heat into the atomic weight, is found to be periodic, rising and falling at regular intervals with increase of atomic weight. (See *Periodic Law*, p. 111.)

Reduction of Pressure. Vacuum.—It has already been mentioned in describing the interior of a laboratory (see Imperial College, p. 25) that nearly all the tables or benches for work are provided with water pumps, used chiefly for aiding filtration of liquids.¹ For this particular purpose it is not necessary, nor is it desirable, to arrange for a very great reduction of atmospheric pressure beneath the filtering surface, which is almost always formed of paper, supported by a glass funnel or by a perforated disc of porcelain. The water-pumps used for this purpose are supplied with high pressure water, and their action is very similar to that of the steam injector.

Two forms of these pumps are shown diagrammatically in Fig. 32 *a* and *b*. In both a jet of water under pressure escapes from the downward-pointed nozzle, and is discharged into the open end of the tube below, carrying with it air drawn from the space to be exhausted by means of the side tube.

The other form of water pump does not depend on the pressure produced by a head of water, but on another principle which requires the pump to be situated at a height a little greater than 30 feet above the surface of the earth or the well into which water falling down a vertical pipe is discharged. The apparatus was first described by Dr. Hermann Sprengel just seventy years ago. If mercury is the liquid used, then the fall pipe requires to be a little over the ordinary height of a barometer, or some 33 or 34 inches, and in this form the Sprengel pump was the parent of some of the more complicated instruments devised later for the purpose of removing air from an enclosed space. These mercurial pumps have played a large part in the modern researches on the gaseous state. The principle is so simple and yet so very important that a description of Sprengel's pump, in the inventor's words,² may be introduced here, as it will enable the reader to understand immediately its more recent modifications. The construction and use of the water pump also becomes obvious.

¹ In many modern laboratories individual pumps are not provided, but a vacuum main, connected to a large mechanical pump, is laid on to the benches, and suction is available simply by turning a tap. This system, although apparently attractive, has many drawbacks.

² *Journal Chem. Soc.*, Vol. 18, p. 10 (1865).

"C *d* is a glass tube longer than a barometer, open at both ends, and in which mercury is allowed to fall down, supplied by the funnel A with which the tube is connected at C. The lower end *d* of this tube dips into a small glass bulb B, into which it is fixed by means of a cork. This glass bulb has a spout at its side, situated a few millimetres higher than the lower end of the tube C *d*. The first portions of mercury which run down will consequently close the tube and form a safeguard against the air, which might enter from below if the equilibrium should be disturbed. The upper part of C *d* branches off at *x* into a lateral tube to which the receiver R is affixed. As soon as the stop-cock at C is opened and the mercury allowed to run down, the exhaustion begins, and the whole length of the tube from *x* to *d* is seen to be filled with cylinders of mercury and air having a downward motion. Air and mercury escape through the spout of the bulb B, which is above the basin H, where the mercury is collected. This has to be poured back from time to time into the funnel A, to pass through the tube again and again until the exhaustion is completed. As the exhaustion is progressing it will be noticed that the enclosed air between the mercury cylinders becomes less and less, until the lower part of C *d* presents the aspect of a continuous column of mercury about 30 inches high. Towards this stage of the operation a considerable noise begins to be heard similar to that of a shaken water-hammer, and common to all liquids shaken in a vacuum. The operation may be considered completed when the column of mercury does not enclose any air, and when a drop of mercury falls upon the top of this column without enclosing the slightest air bubble. The height of this column now corresponds exactly with the height of the column of mercury in the barometer; or what is the same, it represents a barometer whose Torricellian vacuum is the receiver R."

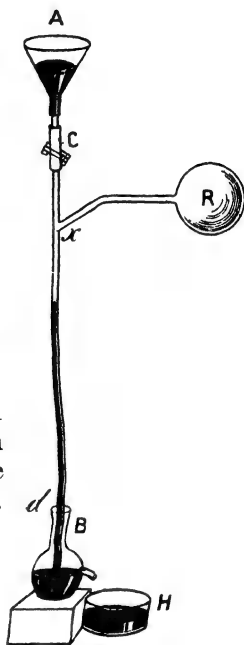


FIG. 33.
SPRENGEL'S MERCURY
PUMP

As a matter of fact the pump in this very simple form does not give a perfect vacuum, for air adheres to the surface of the glass funnel and tube, and india-rubber joints do not exclude the entrance of minute quantities of air. The mercury requires to be admitted to the fall tube with greater precaution, and the whole must be constructed of glass without rubber connections. Figure 34 shows a pump of this kind as mounted in the late Sir William Crookes's laboratory. It will be seen that there are four fall tubes, down which the mercury drops as it is supplied from the reservoir at the side when the latter is lifted to the proper height. There is a vertical tube placed alongside the fall tubes, and this standing in a vessel of mercury acts as a barometer, and so indicates by the height of the mercury the first stages of the exhaustion. The apparatus shown includes a Plücker tube in which gas under examination can be illuminated by the electric discharge, and the light viewed through a spectroscope, of which the end bearing the slit appears on the left.

Another form of mercury pump was devised by Töpler, and was once frequently used for laboratory purposes. A cylindrical vertical vessel is connected at its upper end with an erect straight glass tube, longer than a barometer tube, and dipping into a basin of mercury. The lower end of the cylinder has a branch which is connected with the vessel to be exhausted, and also, by means of a flexible rubber tube with a reservoir of mercury. When the reservoir is raised the mercury rises into the cylinder and cuts off connection with the vessel from which the air is to be withdrawn. On continuing to raise the reservoir the mercury rises and drives all the air out of the cylinder into the barometer tube, expelling the excess of it from the bottom of that tube. On lowering the reservoir again the mercury retreats, but the only air which can take its place in the cylinder is that which is drawn from the vessel to be exhausted. The mercury thus plays the part of a piston which moves up and down in the cylinder, and by repeating the operation a sufficient number of times the air within can be expanded indefinitely, and ultimately a very good vacuum can be obtained.

Modified forms of the Töpler pump were used by Sir J. J. Thomson in his classical work on the electron (p. 102) and by the late Lord Rayleigh in his studies of gas density which led eventually to the discovery of the inert gases of the atmosphere (p. 122). Although capable of giving a good vacuum the operation of these

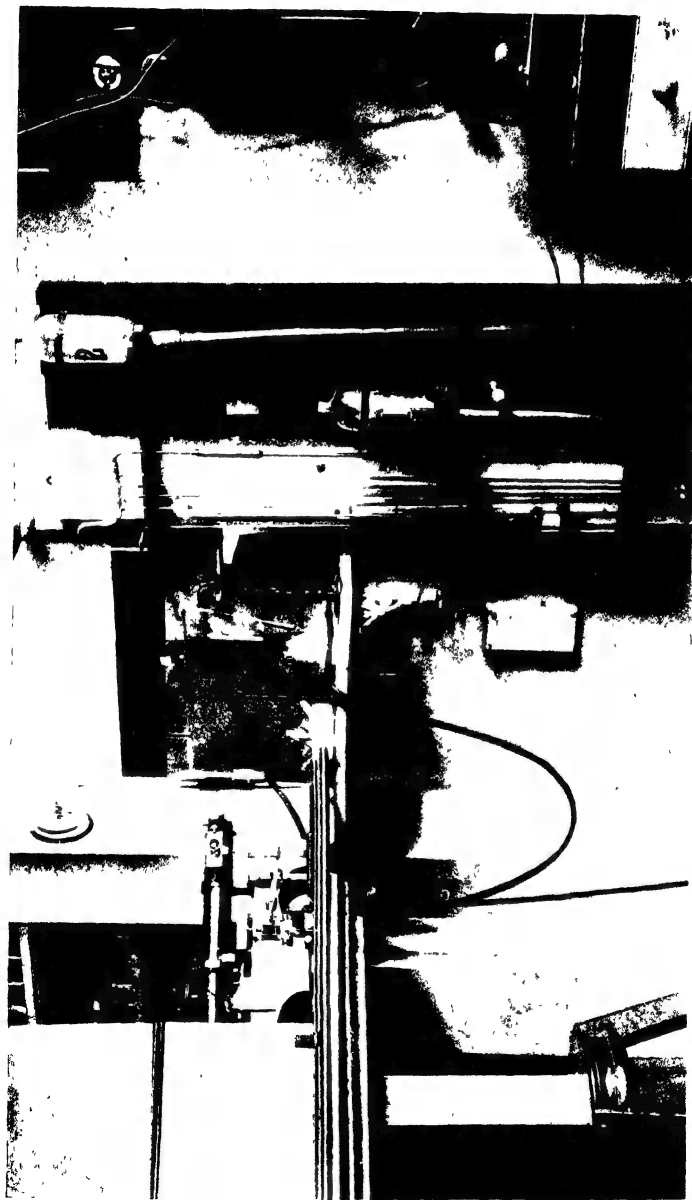


FIG 34 --SPRENGEL PUMP IN SIR WILLIAM CROOKES' LABORATORY

pumps is very tedious, since the reservoir has continually to be raised and lowered, and it is recorded that Lord Rayleigh spent a whole morning in evacuating a 2-litre globe; the same process could be carried out in a few seconds with a modern pump!

Where a very high degree of evacuation is required it is customary at the present time to use some form of "molecular" pump which has no moving parts; this type of pump was first described by Gaede in 1915, and a very satisfactory form of it, designed by Dr. Irving Langmuir of the General Electric Company of America, known as a "condensation" pump, has become popular. In this pump mercury or a special oil is heated in one portion of the apparatus and condensed in another; between these two parts the mercury or other vapour rushes at high speed and in doing so drags air, or other gas, with it from the vessel to be evacuated. This gas has to be removed by another pump of a less powerful nature, known as a "fore" or "backing" pump; the latter is generally some form of mechanical rotary pump run by an electric motor. It is stated that, with the aid of a good fore-pump, a Langmuir pump is capable of evacuating down to a pressure of a millionth part of a mm. of mercury at the rate of 3000 c.c. or more per second; this may be compared with the rate of evacuation, at little less than a ten-thousandth of a mm., of 0.5 to 5 cc. per second for a Sprengel pump, and 0.35 c.c. per second for a Töpler pump at a pressure of about a hundred-thousandth of a mm. of mercury.

A very valuable method of obtaining a high vacuum without the use of a pump has been introduced by Sir James Dewar. It has long been known that charcoal absorbs many gases very freely, and this property has been turned to account for many practical purposes in past times. Thus a respirator, consisting of a small metal case filled with coarsely crushed wood charcoal, which could be held over the mouth and nose, was actually in use by nurses and dressers before the days of antiseptic surgery.

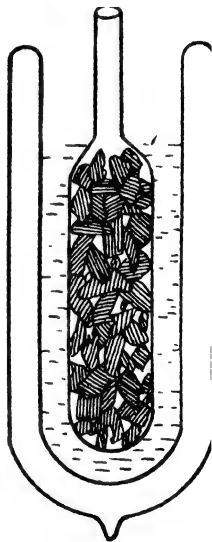


FIG. 35.
CHARCOAL VACUUM
VESSEL

Such an appliance also protects the wearer very completely for a short time if exposed to an atmosphere containing irritant fumes. The most dense varieties of charcoal, obtained for example by heating cocoanut shell, seem to be the most efficient. If a glass vessel filled with charcoal of this kind is first heated, and the moisture and gases removed by means of a mercury pump, and the vessel is then connected with the space to be exhausted and immediately plunged into a vacuum vessel containing liquid air, the gases present are absorbed with great rapidity and completeness. A selection is made by the charcoal when exposed to contact with mixed gases, air, oxygen and nitrogen are absorbed more readily than hydrogen, while helium and neon remain unabsorbed to the last.

In most chemical laboratories reduced pressure is used only for the distillation of liquids which normally decompose on boiling and the high degree of vacuum given by a molecular pump or by charcoal in liquid air is not necessary, whereas that of the water-pump (about 7 mm. under the best conditions) may not be sufficient. For such purposes rotary oil pumps, similar to the one introduced by Gaede in 1907, are now frequently employed; they are driven by an electric motor at a speed of about 500 revs. per minute, and are capable of evacuating down to a pressure of one-hundredth of a mm. of mercury without the aid of a fore-pump.

Electrolysis.—In the chemical laboratory the electric current is used in two directions, namely, in the production of heat as already described, and for its application to electro-chemical decomposition for analytical and other experimental purposes. In the latter case in all ordinary operations a small current of 10 to 15 ampères is all that is necessary. The current is usually obtained from a battery of accumulators of 12 to 24 cells, which can be charged from the electric lighting circuit. Four cells will usually furnish each working place, which is fitted with suitable resistances, an ammeter for measuring the current, and a voltmeter.

In ordinary gravimetric analysis the weight of some precipitate of known composition formed in the liquid by adding a suitable reagent is the object aimed at. Take, for example, a solution of copper sulphate of which it is desired to know the amount. If to one-half of the solution an excess of solution of caustic potash is added and the liquid is heated to boiling, a black

precipitate of copper oxide is formed, which is then collected on a paper filter, washed by pouring hot distilled water over it, then dried completely, and after heating to redness it is weighed. From the known composition of the copper oxide, CuO , the amount of copper is calculated.

Similarly if a solution of barium chloride is added to the other half of the solution a white precipitate of barium sulphate is produced. If this precipitate is in corresponding fashion collected, washed free from the copper solution, dried, ignited, and weighed, the amount of the sulphur, SO_4 , present in the original solution can be calculated from the weight of barium sulphate obtained in the form of the precipitate, and thus the total weight of copper sulphate in the original solution becomes known.

In electro-analysis, which in many cases is more rapid and more exact, the metal in a metallic salt is deposited as such by the action of an electric current on a weighed plate or gauze of metal which can be used as the cathode in the process. In modern processes for rapid electro-deposition of metals one or other of the electrodes is made to revolve rapidly in the solution under analysis. The advantage of this is obvious from the consideration that in decomposing, say, a solution of a copper salt, the liquid in the neighbourhood of the cathode surface becomes impoverished as the metal is deposited upon it, and unless the liquid is stirred so as continually to bring fresh solution into contact with the cathode, the operation occupies a considerable length of time, as the extraction of the last portions of metal is then dependent on convection currents bringing those portions of the solution which still contain copper into contact with the cathode. The electrodes should be as close together as possible, and warming the solution is often an advantage. It appears to be of no importance whether the anode or the cathode be made to revolve, or whether the electrodes are stationary, the stirring being accomplished by an independent stirrer. With suitable arrangements the estimation of a metal such as copper, once in solution, can be accomplished in a very short space of time, not exceeding a few minutes.

The arrangement for the use of rotating electrodes is shown in Fig. 36, p. 80.

By suitable gradation of the potential used two metals such as copper and zinc may be deposited one after the other from the same solution.

The current may also be employed for many experiments in which the oxidising effect at the anode, or the reducing effect at the cathode, may be turned to advantage. This method has been employed chiefly in connection with the study of organic compounds. The solution is divided into two parts by a porous partition, the cathode being on one side, the anode on the other, both being immersed in the same solution, the substance to be operated on being dissolved in the one compartment or the other according to the effect, reduction or oxidation, which it is intended to bring about.

The Spectroscope is an instrument now familiar and to be found in some form in every chemical laboratory. The discovery that white light is made up of a great number of rays which give to the eye the sense of colour, was made by Newton at some time previous to the year 1675, when he described many experiments, and gave the explanation of them in his treatise on "Opticks" presented to the Royal Society. But the application of this discovery to the purposes of the chemist and physicist came nearly two hundred years later, when the spectroscope was invented and used by Bunsen and Kirchhoff, professors at the University of Heidelberg. Newton discovered that lights which differ in colour, differ in refrangibility,¹ and when a beam of white light passes through a transparent prism the coloured rays of which it is composed are spread out, and when received on a white screen exhibit a coloured band called the spectrum. In order that the coloured rays may not overlap and confuse one another the light should be made to pass through a narrow slit parallel with the edges of the prism. The spectroscope then is an instrument consisting of one or more prisms, through which the light is made to pass, and by which the coloured rays are separated and dispersed. The light to be examined is admitted through a slit and passes, on its way to the first face of the prism, through a lens fixed in a tube, called the collimator, by which the rays are rendered parallel. The spectrum produced by passage through the prism is observed through a telescope movable through a small arc so as to enable the observer to see

¹ The refrangibility of light, generally stated as the "refractive index," is a measure of the extent to which the light is bent out of its course, or refracted, when it passes from one medium, e.g. air, into another, e.g. a glass prism or a transparent liquid.

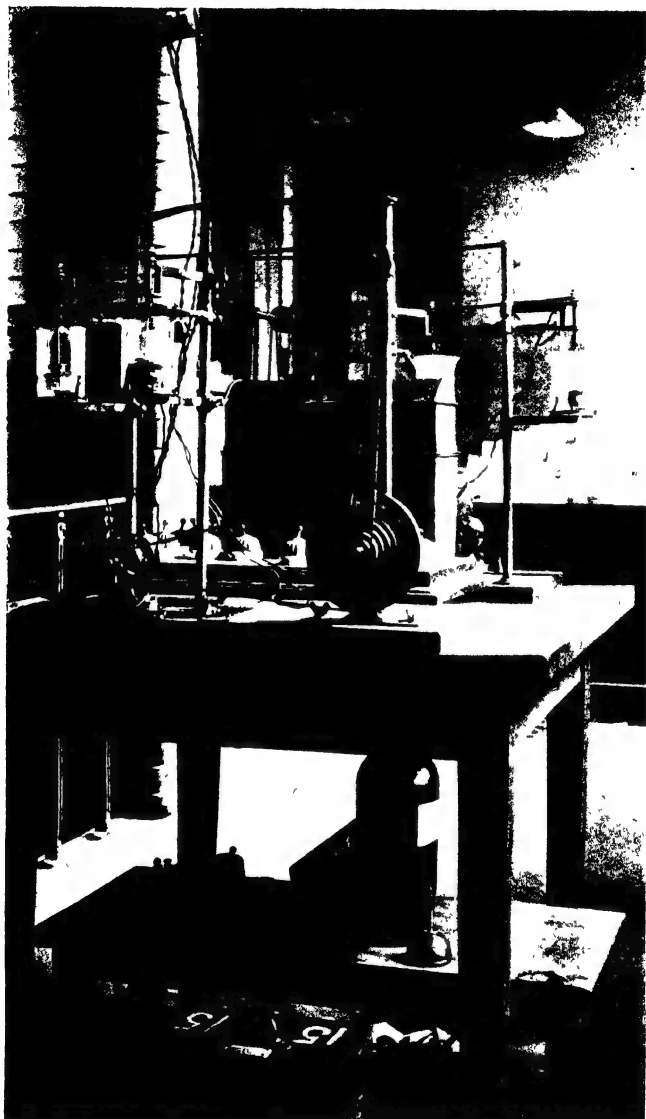


FIG 36 —GOVERNMENT LABORATORY
APPARATUS FOR ELECTRO-ANALYSIS

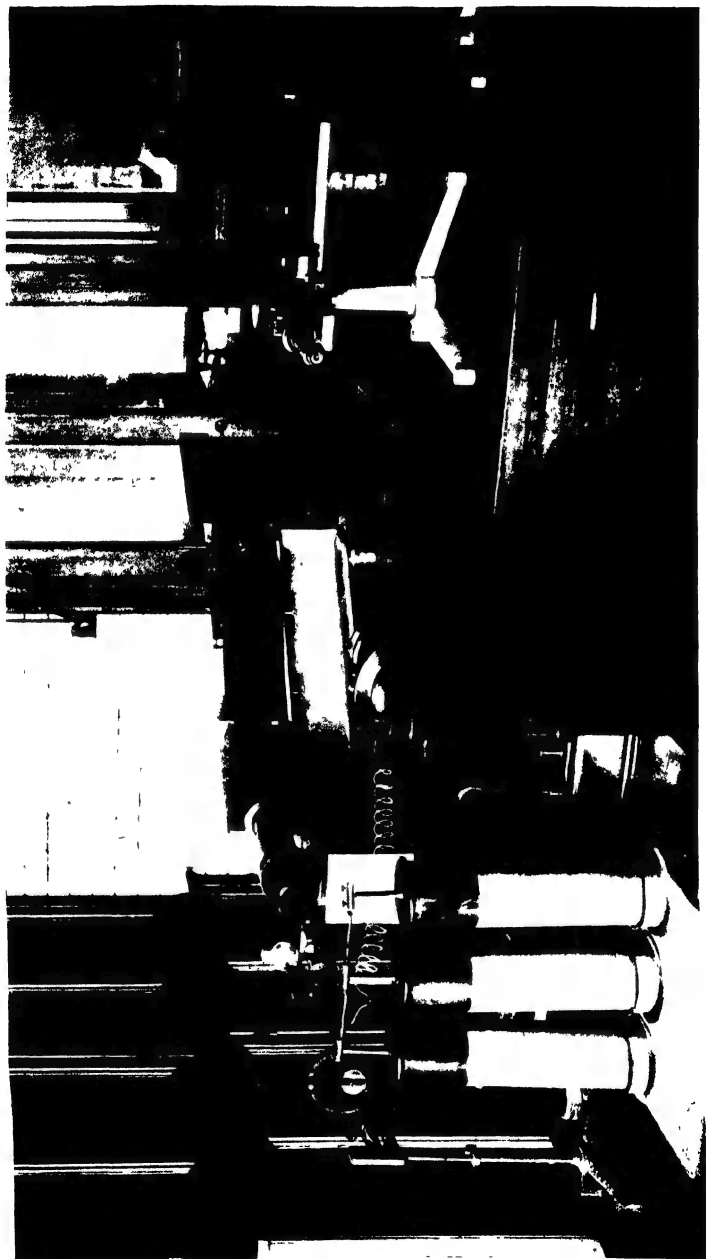


FIG 37 — GOVERNMENT LABORATORY SPECTROSCOPE ROOM

either the less refrangible rays at the red end or the more refrangible blue. The eye of the observer is sometimes replaced by a photographic plate on which the spectral lines or bands are recorded. In Fig. 81 is shown a spectroscope with one prism, and a large instrument with several prisms. The latter has a camera attached to the telescope and at the other end, next the slit, is an arrangement for producing electric sparks or a discharge through a tube containing gas or other materials which when thus treated emit light.

The spectroscope has been used for such purely academic studies as the determination of the composition and other properties of stellar bodies, and the investigation of the structures of atoms and molecules, as well as for the more practical object of analysing substances of unknown composition.

Other instruments are required for special purposes. The *Refractometer* is an instrument for determining the refractive index of transparent substances; it finds application in the examination of animal and vegetable oils and fats, and for other analytical purposes. The refractive index is often used to calculate the "molecular refractivity" of a substance, since this has a special theoretical significance.

The *Polarimeter*, of which there are several forms, is used for measuring the angle through which the plane of polarisation of a ray of polarised light is turned, to the right or left, when the light is made to traverse a layer of known thickness of a substance which has the property of circular polarisation. This instrument is much used in connection with the study especially of organic compounds (see Stereo-chemistry), and it is almost always applied to liquids. Solids which have to be examined are dissolved in an appropriate solvent. Substances containing sugar are almost invariably analysed by means of the polarimeter.

The *Microscope* is occasionally used for examination of precipitates or other fine powders to ascertain if they exhibit crystalline structure, but it is most frequently employed in the study of micro-organisms, especially in connection with fermentation. In the metallurgical laboratory the microscope is much used in the examination of steel and other metals.

The *Colorimeter* is an instrument by which a comparison can be made between the colour or depth of tint of some liquid and a column of equal length of a standard solution. This com-

parison is often applied to the case of drinking water, and affords a useful indication of contamination by organic matter derived from the surface drainage of land or from streams which have passed through peaty or other vegetable deposits.

The Goniometer is used for measuring the angles of crystals. The instrument in its original simple form was described by Wollaston in 1809. It is much to be regretted that the goniometer is not to be met with in many chemical laboratories. This is perhaps due to several circumstances. Up to comparatively recent times the measurement of crystals has been applied almost exclusively by the mineralogist, for the mere recognition and characterisation of minerals, and the importance of crystal-line form in its relation to chemical constitution has been recognised only within recent years. It is also doubtless in part attributable to insufficient acquaintance with the necessary mathematics, but as the mathematical treatment of chemical problems has become common, the study of crystals would probably have received a larger share of attention from chemical students were it not for the fact that their normal curriculum is already greatly overweighted.

X-ray apparatus is finding increasing use in both research and industrial laboratories : its applications fall into three categories : (1) It will be seen subsequently (p. 102) that X-rays are formed whenever cathode rays, produced in a vacuum discharge tube, strike matter. The wave-lengths of the rays depend on the nature of this matter, and each element gives a unique and characteristic set of rays, so that by this means it is possible to detect the presence of any element. In fact the study of the characteristic X-rays has been employed to prove the presence of new and hitherto unknown elements ; the X-ray method is now regarded as the most reliable of all analytical processes in the hands of a skilled worker. (2) The transparency of matter to X-rays is well known and this property is utilised to investigate metallic castings and weldings for interior defects. (3) Like light, X-rays can be "diffracted," that is to say the rays after being reflected from matter are capable of enhancing or interfering with one another, so as to produce a definite diffraction pattern. From a study of these patterns information can be obtained concerning the fundamental structure of matter ; the X-rays have in this connection been compared to a super-microscope.

Since X-rays are themselves not visible to the eye, they can, of course, best be studied by their effect on a photographic plate.

In conclusion mention must be made of the application of fused silica or quartz glass to the construction of chemical apparatus. This substance melts at about the same temperature as platinum, and is manufactured in two qualities, opaque and transparent. The former is made in an electric furnace from the less pure varieties of massive quartz; the amount of impurity is, however, very small, not usually exceeding $\frac{1}{2}$ per cent, the opacity being due to air bubbles. Muffles, trays, and large evaporating dishes are made of this material, as it resists the action of all acids except hydrofluoric acid, and, at high temperatures to a small extent, phosphoric acid. The transparent silica ware is made from rock crystal, and for some years was made exclusively by fusion in an oxyhydrogen flame. Small flasks, beakers, tubes, crucibles, dishes, and other vessels are now in use in all laboratories with great advantage, owing to the remarkable properties of this substance in relation to heat and chemical agents. Its coefficient of expansion being very small, only about $\frac{1}{17}$ that of common glass, a silica vessel bears sudden changes of temperature without damage. It is an interesting and surprising experiment to see a silica flask heated to redness in a flame plunged at once into cold water without a crack.

At the same time it is not advisable to subject large or thick masses of the material to so severe a test. And of course it must be remembered that although silica resists the action of ordinary acids it is not proof against alkalis. Contact with hot alkaline solutions and especially fused potash or soda and lime or baryta must be avoided.

PART II

MODERN DISCOVERIES AND THEORIES

CHAPTER IV

PRINCIPLES OF CHEMISTRY

CHEMISTRY is a science based on the results of experiment, but its real foundation belongs to quite modern times when experiment began to take the form of exact measurement. For ages all kinds of chemical operations and manufactures had been practised in a crude way, such as the production of soap, glass, dyes, and pigments, the distillation of alcohol from wine, the production of sulphuric acid from green vitriol, and so forth.

It was only in the middle of the eighteenth century when Black, and a little later Lavoisier, began to weigh and measure, as accurately as they could, the materials with which they were working or the products obtained in their experiments, that a body of facts was gradually accumulated on which theories could be safely established.

At different periods in the history of the science various estimates have been formed as to the influence of different men or the importance of different discoveries. Many writers have been accustomed to date the rise of chemistry as a branch of science from the time of Robert Boyle, "The Father of Chemistry" as he has been called, at the end of the seventeenth century.

Boyle gave the first clear and precise idea of the word *element* so much used in chemistry. For he got rid not only of the Aristotelian four elements, but of the whole brood of fantastic assumptions which for centuries had clouded the brains of the alchemists. Their *tria prima*, the salt, sulphur, and mercury of their occult lore, were henceforth to disappear, and the elements of the chemist were simply those substances which were found to be incapable of further analysis.

An eminent French chemist, Wurtz, about seventy years ago commenced a graphic history of chemical theory with the words "Chemistry is a French science. It was founded by Lavoisier of immortal memory."

For such a statement, if we make allowance for a little exaggeration arising out of not unnatural national pride, justification would be sought in the interpretation of the facts then accumulated about combustion and the overthrow of the then prevalent doctrine of "phlogiston" which science owes to the genius of Lavoisier. The classification of acids, bases, and salts, and the system introduced in his remarkable *Traité élémentaire de Chimie*, as well as the nomenclature which in principle is used, so far as it is applicable, down to the present day were also part of his work.

By some English writers, on the other hand, John Dalton in virtue of his "Atomic Theory" has been regarded as the real founder of the modern science. For this view there is some justification, for the conception introduced by Dalton in 1808 remains to this day the indispensable foundation on which all modern chemistry is built, and without which some departments of our science, notwithstanding the accumulation of facts, would either not exist at all, or would remain a chaotic assemblage of observation and hypothesis.

Whatever may be the verdict about the claims of these older men of science as founders of modern chemistry there have been undoubtedly epochs from which a new departure may be dated. One of these, inaugurated about 1860, arose out of the belated recognition of a principle enunciated clearly enough fifty years before by the Italian physicist Avogadro.

It was a countryman of his, Cannizzaro, for the last forty years of his life professor of chemistry in the Royal University of Rome, who with remarkable insight perceived the importance of Avogadro's hypothesis, and with most praiseworthy insistence persuaded the chemical world of 1858 to listen to his expositions. The principle will be explained a little later.

About this time also began the more systematic study of the physical properties of substances in connection with the enquiry into their composition which had been previously the chief business of the chemist. The melting points, the boiling points, the specific gravities, the optical properties of bodies henceforward occupied attention, and it was by observations of one of these properties, namely, the power possessed by many substances of rotating the plane of polarisation of a ray of polarised light, that one of the most fruitful discoveries of our time was made. The first observations on the fact that for

every compound which possesses the power of turning the plane of polarisation to the right, there is another which, while possessing the same composition, rotates equally to the left, was made by Pasteur in 1848 when a very young man. His discovery of the relation between the crystalline forms of the several tartaric acids and their action on polarised light led him to perceive the necessity for some kind of theory to account for the internal structure of the molecules of such compounds. If the atoms composing the molecule in one of such a pair of compounds be conceived as arranged in a particular order, then the atoms in the other must be arranged in the same order but inversely, so that if the atoms could be made visible they would be seen to exhibit the relation of an object to its image in a mirror. Twenty years later the subject again attracted attention, and after the study of the lactic acids by Wislicenus, a theory was put forward, by the Dutch chemist Van't Hoff, and the French chemist Le Bel, which furnished the necessary clue, and provided the basis for that large department of the subject which has since developed so remarkably under the name "Stereo-chemistry," or chemistry in space.

But probably nothing has contributed more to the progress of modern chemistry than the closer study of the relations of chemical to electrical phenomena. The fact of the decomposition of water by the voltaic pile in 1800 was soon followed by the isolation of the metals potassium and sodium by Davy, and later the establishment of the quantitative laws of electrolysis by Faraday. Then came all the wonders of spectral analysis, and so the still greater wonders to be revealed by the phenomena connected with the discharge of electricity through attenuated gases were not discovered till a good many years later.

Another circumstance which has greatly assisted progress in chemical research is the development of many of the improved instruments which are now available for the use of the experimenter. Some of these have been already described and the invention of the Sprengel mercury pump in 1864, by which a high vacuum was for the first time easily available, was certainly one of them. So also is the development of the dynamo by which an electric current is now supplied to every laboratory, and made accessible for so many purposes formerly undreamed of. Thus operations in which the current is made to produce

chemical decomposition, or electrolysis, may be the object on one occasion, while on another a high tension discharge through a so-called vacuum tube may be wanted or the production of an arc for experiments at high temperatures. Machines for the liquefaction of air and other gases afford, on the other hand, the means of producing great cold, and much has been learned during the last thirty years about the properties of matter at low temperatures, and the influence of temperature on chemical action. The range of temperatures thus attainable in the laboratory stretches from approximately that of interplanetary space to near the surface heat of the sun. Many manufacturing operations are now conducted at the temperature of the electric arc, such as the production of calcium carbide, the manufacture of phosphorus and carborundum, the fusion of quartz for making silica vessels, and the reduction of several metals from their oxides.

Among the most remarkable results of the application of modern theoretical ideas should be remembered the success which has attended the production of organic compounds, many of which had been previously known only as naturally occurring constituents of the tissues of animals or plants. The synthesis of alizarin, the red colouring matter of madder, has for many years been conducted on a large scale for industrial purposes, and the synthesis of indigo has already resulted in the almost total extinction of the cultivation of the indigo plant.

Some of the sugars, fats, and nitrogenous constituents of animal matters have in like manner been built up by chemical operations from purely inorganic materials. To this list must now be added two vitamins and at least two hormones, the latter being the active constituents of the secretions from certain glands of the human body. It is also a matter of common knowledge that many of the drugs employed in modern medical practice—saccharin, aspirin, phenacetin, antipyrin, sulphonal, etc.—are artificial products of the chemical laboratory.

In theoretical chemistry electrical ideas are predominant. Chemical combination or decomposition is attributed to exchanges of electrical units, and the decomposition of fluid bodies by the electric current is almost universally attributed to the presence of "ions," wandering free fragments of molecules carrying electric charges. From the discoveries which have been made during the last fifty years by Sir William Crookes

and, especially more recently, by Sir Joseph J. Thomson and his school, coming about the same time as the discovery of radium, we should be perhaps justified in saying that the opening of the twentieth century is a new epoch in chemistry. For in these last few years chemists have had to get accustomed to the idea that the atoms of Dalton, previously supposed to be indestructible, are complex structures all of which can be broken up, some even undergoing spontaneous disintegration.

Leaving generalities we may now give a brief statement of the fundamental principles accepted generally by chemists at the present day, in order that what follows may be intelligible to the general reader.

First of all great principles in which chemistry is concerned is the doctrine of the *Conservation of Mass*. This means that though matter may be transformed in appearance and qualities none of it is lost or destroyed. When a candle is burned it slowly disappears, but when arrangements are made for catching and weighing the gaseous products of its combustion these are found to be made up of the carbon and hydrogen of which the wax is composed, together with oxygen taken from the air. Or when limestone is heated in a limekiln the lime which remains always weighs fifty-six pounds for every hundred pounds of limestone burnt, if the latter is free from impurities. The carbon dioxide, commonly called carbonic acid, which escapes can be shown to represent the missing forty-four pounds, and if combined again with the lime will reproduce the original substance. Experiments of this kind were originally published by Black in 1777.

It is true that elaborate experiments have been made in recent times to test the validity of this principle, but none of the results observed so far have shaken confidence in its soundness (see, however, p. 97).

The practice of weighing carefully led to the discovery, early in the nineteenth century, of the *Law of Constant Proportions*. Here again is a fundamental principle. The law states that any given chemical compound is always composed of the same elements united in the same proportions. This proposition was finally established by a French chemist, Proust, early in the nineteenth century, notwithstanding much controversy and criticism. It is of course a principle on which rests the whole of quantitative analytical chemistry, and from the practice of

which daily evidence of its truth is supplied. In plain language it means that, for example, water is always composed of one part of hydrogen combined with eight parts of oxygen, and that no matter from what source it is procured it always has exactly the same properties, the same colour, the same boiling point, the same freezing point.¹ If different samples of natural water seem to differ one from another, as, for instance, rain water from river or sea water, this is merely due to the presence of other substances dissolved in it, and which by well-known methods can be separated from it, leaving the water unchanged.

Another important law in chemistry is the *Law of Multiple proportions* discovered by John Dalton, and illustrated and explained by his famous *Atomic Theory*.

The question whether matter is capable of division and subdivision *ad infinitum*, or whether there is a limit beyond which the particles are so hard that no power in nature is capable of breaking them into smaller pieces, is one which has been debated from the earliest times.

The vague atomic hypothesis of Democritus was the subject of fruitless debate in the Middle Ages. Newton in expounding his gravitation theory, which is applicable to the smallest particles of matter as well as to the suns and planets, gave expression to the view that in the beginning matter was formed of "solid, massy, hard, impenetrable, movable particles," and that "those primitive particles being solids are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces." But it was reserved for Dalton to supply that basis of fact without which every hypothesis is useless. How the theory was established is explained in the best text-books. It will be sufficient here to give in Dalton's own words an enunciation of the modern doctrine.² "Chemical analysis and synthesis go no farther than to the separation of particles one from another and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. . . . All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those

¹ This statement of the absolute constancy in properties of water requires some modification in view of the discovery of a heavier form (isotope) of hydrogen (see p. 151). The idea of *constant proportions*, namely, that every molecule of water contains two atoms of hydrogen and one of oxygen, still rigidly holds good.

² *Dalton's Chemical Philosophy*, 1808, Vol. I, p. 112.

that were previously at a distance." If, therefore, there are two substances which can combine, say nitrogen and oxygen, their union can only occur between whole numbers of atoms, such as one atom of nitrogen to one atom of oxygen, one atom of nitrogen to two atoms of oxygen, or two atoms of nitrogen to one atom of oxygen, etc.

The stable compounds of nitrogen with oxygen are represented by the following formulæ in which each of the capital letters represents one atom of the element :

Nitrous oxide	N_2O
Nitric oxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide	N_2O_4
Nitrogen dioxide	NO_2
Nitrogen pentoxide	N_2O_5

Obviously if the weight of matter represented by each symbol is known, the relative weights in which the two elements combine to form these compounds is also known. The weights attributed to the symbols are called the atomic weights, and what has been learnt about them since Dalton's time will be discussed at length in later pages.

No sooner is the conception of the atom as the ultimate particle of an element firmly established than it becomes obviously desirable to use some other word to designate the pile of atoms, which, according to the theory, is formed when a chemical compound is produced. Such a word is *molecule* (dim. of Latin *moles*, a heap) which, though introduced into science more than a century ago, has only become during the last seventy years both familiar and endowed with a precise signification. Dalton himself did not scruple to write of an atom of water, and made no distinction between an atom of an element and an atom of a compound. And in one sense this is justifiable, for what is now called a molecule of water is also an atom (i.e. something indivisible) inasmuch as if further divided it ceases to be water, and becomes a mixture of oxygen and hydrogen.

The word molecule acquired serious importance when it appeared in the title of a paper published in 1811, which, though it attracted comparatively little notice at the time, was at last recognised by the chemical world so long afterwards as 1860.

This was the paper by the Italian physicist, Avogadro,¹ in which is enunciated the hypothesis which bears his name, and which is expressed as follows: "Equal volumes of gases, simple or compound, contain under the same conditions of temperature and pressure the same number of molecules." Hence the weights of gaseous molecules are directly proportional to the specific gravities of the gases. And from the known densities of the elementary gases it follows that many of them consist of molecules containing more than one atom, e.g. hydrogen, oxygen, nitrogen, chlorine contain two atoms each.

The determination of the density of the vapours of a large number of substances which, though not gaseous at common temperatures, are convertible into vapours by heat, provides, therefore, a method very generally applicable to the determination of molecular weights.

A molecule is now always understood to mean the smallest mass of any substance, elementary or compound, which is capable of existing by itself.

At the time of the publication of Avogadro's hypothesis, or law as it is often called, Michael Faraday was a youth just twenty years of age, and as yet following his occupation of bookbinder. It was only little more than twenty years later that, pursuing the study of electro-chemical decomposition or electrolysis, he gave the world the two great quantitative laws which are generally known as Faraday's Laws of Electrolysis. They may be stated as follows in his own words, which will be found in his *Experimental Researches in Electricity* (vol. I, p. 241):

I. "The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

II. "Compound bodies may be separated into two great classes, namely, those which are decomposable by the electric current, and those which are not. . . . I propose to call bodies of the decomposable class *electrolytes*. Then again the substances into which these divide under the influence of the electric current form an exceedingly important general class. They are combining bodies, are directly associated with the fundamental parts of the doctrine of chemical affinity, and have each a definite proportion in which they are always evolved during

¹ The reader who is interested in such matters as the history of Avogadro's doctrine should read the "Memorial Lecture on Cannizzaro," by Sir Wm. Tilden, in the *Transactions of the Chemical Society* for 1912, p. 1677.

electrolytic action. I have proposed to call these bodies generally, *ions*, or particularly *anions* and *cations*, according as they appear at the *anode* or *cathode*, and the numbers representing the proportions in which they are evolved *electro-chemical equivalents*. Thus oxygen, chlorine, iodine, hydrogen, lead, tin are *ions*; the three former are *anions*, hydrogen and the two metals are *cations*, and 8, 36, 125, 1, 104, 58 are their electro-chemical equivalents nearly."

The theory by which the process of electrolysis is now explained has been very considerably modified within recent times, but Faraday's two quantitative laws remain unaltered, and constitute a firm basis on which researches continued since Faraday's time securely rest.

In the meantime almost before Dalton's Atomic Theory had become familiar to the majority of chemists, and long before Faraday's discoveries in electricity were made known, another discovery was made, the importance of which has in later times been fully recognised. In 1819 the two French physicists, Dulong and Petit, discovered the relation between specific heat and atomic weight,¹ which can be stated as follows: the specific heat of an element in the solid state is inversely proportional to its atomic weight.

Consequently the number expressing the specific heat, multiplied by the atomic weight, gives a constant which is approximately 6.4 for all temperatures between the freezing and boiling points of water. Four exceptions among the elements, namely, carbon, boron, silicon, and the metal beryllium are known, but are accounted for, and the principle is universally accepted and acted upon for the purpose of regulating the value to be assigned to those atomic weights which cannot be fixed by appeal to other rules, such as that of Avogadro.

Dulong and Petit expressed their law in the following words: "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur." That is, the atoms of all the elements have exactly the same capacity for heat.

An equally remarkable fact was observed some years later by Neumann, who found that there was a similar relation between the specific heats of chemically similar compounds, and the sum

¹ Atomic weights represent the relative weights of the atoms of different elements; it is usual to take the atomic weight of oxygen as 16.00, as a basis of comparison (see p. 109).

of the atomic weights of the elements composing them. Since that day these results have been corrected and extended, so that it may now be said that the specific heat of the molecule of a compound is, very approximately, the sum of the specific heats of the atoms composing it. In other words the capacity of the elementary atoms for heat is the same whether they are in the elemental, uncombined state or form part of a chemical compound. The independence of the atom in any condition is the interesting point.

Down to quite the end of the eighteenth century it was supposed that heat was a kind of substance which existed in all sorts of matter and was squeezed out of it when subjected to pressure or friction. The material of heat was called *caloric*, and when associated with certain kinds of matter in sufficient quantity the liquid or gaseous state was produced. Lavoisier, for example, spoke of oxygen gas as made up of the basis of oxygen combined with caloric. But very soon after this time Rumford showed that a given mass of any metal, such as brass, can give out heat in indefinitely large quantity when subjected to friction in the process of boring. Sir Humphry Davy a few years later demonstrated that ice can be melted by merely rubbing it, though kept all the time in an atmosphere below the freezing point of water. Finally, in 1843, Joule of Manchester showed that there is a quantitative relation between the work done by a body falling under the influence of gravity and the heat which is produced in the process. Joule's experiments led to the result that a mass of 772 lbs. falling through 1 foot or of 1 lb. falling through 772 feet may produce, by friction or otherwise, heat enough to raise the temperature of 1 lb. of water 1° Fah. This expresses in ordinary English weights and measures the *mechanical equivalent of heat*. It may be expressed in grams, metres, and degrees centigrade, or otherwise, and the work done by the falling mass, attracted by the earth, may be utilised either to produce heat by friction directly, or it may first produce an electric current which may then be converted into heat, but the same quantitative relation is maintained. Hence we have the theory that heat is a "mode of motion" and that this motion is convertible into heat, light, electricity or magnetism, production of steam, and so mechanical force, or finally into chemical action. In any one of these cases the body concerned is said to possess *energy*, and the work it can do while changing

its state is a measure of the amount of energy available. The energy of a body in motion is what is called *kinetic energy* (κινέω, to move), while that which it owes to its position or chemical state is called its *potential energy*. The one being convertible into the other, the sum of these two quantities is constant. These facts have been studied from many sides by a large number of physicists and engineers, beside those whose names have already been mentioned. Among those of the past are the names of Carnot and Meyer, while those of Helmholtz, Kelvin, Maxwell, Clausius, and Willard Gibbs belong to more recent times. And the sum of their work is the principle of the *Conservation of Energy* which, with the *Conservation of Mass*, lies at the foundation of chemistry.

During the past thirty years it has become evident that the two concepts of conservation are not independent, and that the ideas of the nineteenth century require some slight modification. In 1905, Einstein, in the course of the development of the theory of relativity, showed that the mass of a body depends on the amount of energy it contains, there being a definite equivalence of mass and energy. In the burning of a candle it is not strictly true to say, as has been already implied, that the mass of the products of burning is *exactly* the same as that of the wax used up and the oxygen taken from the air; the final mass is actually less than the original by an amount equivalent to the energy given out in the form of light and heat. This quantity is, however, so minute as to be quite unweighable even on the most sensitive micro-balance yet constructed, so that for all practical purposes the laws of conservation of mass and of energy may be applied independently in their simplest forms, without taking the equivalence of energy and mass into consideration. But in connection with the problems of atomic disintegration and the genesis of the elements (chapter VIII) this equivalence is of great importance.

CHAPTER V

ELECTRIC DISCHARGE IN GASES

THE smallest part of any substance capable of independent existence is called a molecule, and according to Avogadro's law already quoted the number of molecules in a given volume of any gas, under like conditions, is the same, and is independent of the composition of the gas. It requires a little thought to realise how tiny are these particles and how many there are crowded together in any small portion of a gas. In gases also they are much further apart than in a liquid or solid. As to their size no better idea can be conveyed than in the words of Lord Kelvin in a lecture at the Royal Institution in 1883. He says : " To form some conception of the degree of coarse-grainedness indicated imagine a globe of water or glass, as large as a football (or say a globe 16 centimetres diameter) to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be more coarse-grained than a heap of small shot but probably less coarse-grained than a heap of footballs."

To express their number in any visible portion of matter is even more difficult. But as the result of



FIG. 38.

SQUARE CENTIMETRE

A cubic centimetre is the volume contained in a cube each face of which is 1 square centimetre.

of different methods it may be stated that it has been estimated that 1 cubic centimetre of air under standard conditions, that is at 0° C., and under a pressure equal to 760 millimetres of mercury (approximately 15 lbs. per square inch), contains 2.7×10^{19} molecules. The highest attainable vacuum still contains many

millions per cubic centimetre.

But the kinetic theory of gases teaches us that in a gas all the molecules are constantly in motion, moving in straight lines, and frequently striking one against another and against the walls of the containing vessel, and so altering their direction. In liquids there is reason to believe that the molecules move but less

actively, and clusters of them move in company, while in the solid state the molecules, though partly fixed, vibrate more or less rapidly about a mean position, the vibration corresponding to what is called their temperature.

It would be easy to confound the reader with large figures if it were attempted to express the velocity at which molecules travel in a gas, or the mass of an atom of hydrogen or oxygen and so forth, but little would be gained. It is only necessary to remember that gas molecules are far too small to be visible with the aid of any known instrument, that they move with great speed and they collide very frequently. The space between one collision and the next is called the free path of a molecule, and though this varies according to circumstances the *mean* free path can be calculated. In its original form the kinetic theory was not concerned with the form or nature of the molecule itself or of the atoms of which it is composed. But within the last thirty years the experimental researches on the phenomena of radioactivity and on the effects of the electric discharge through attenuated gases have supplied information of the most unexpected and startling kind, which may be regarded as giving to physicists and chemists alike an entirely new point of view as to the ultimate constitution of matter.

Soon after the improvement of the induction coil by Ruhmkorff over eighty years ago, experiments on the production of sparks in air and other gases led to the discovery of the beautiful luminous effects which are produced when the discharge passes through gases in an attenuated state. It was discovered, among other things, that the colour and appearance of the light depend not on the substance of the electrodes, but on the nature of the enclosed gas. It was also found by Plücker that the luminous discharge was capable of deflecting a suspended magnetised needle, and is itself acted upon by a magnet.

It will be worth while to begin by a brief account of the principal facts about the electric discharge. If the two terminals of any source of high potential electricity are separated by a gas such as air at common atmospheric pressure, and the voltage is gradually increased, at a certain difference of electric pressure the air is ultimately unable to bear the strain and a current passes momentarily producing a spark. If now the gas contained in the experimental tube is expanded by the use of an air pump, the difference of potential in the two terminals

required to cause a discharge is less, and as the pressure on the gas is diminished the character and appearance of the discharge changes. Straight, well-defined sparks are no longer produced, but a line of light, extending the whole length of the tube, is gradually developed, while the negative pole becomes covered

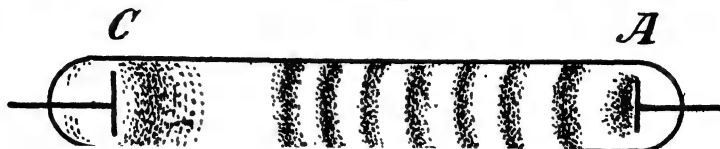
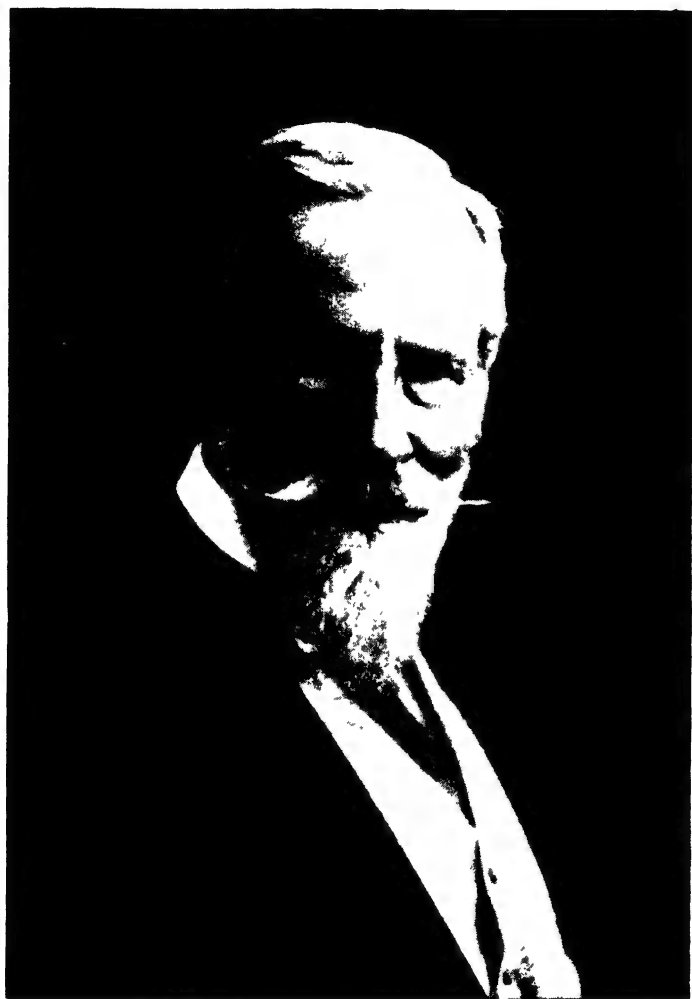


FIG. 39. ELECTRIC DISCHARGE UNDER REDUCED PRESSURE
C = Cathode A = Anode

with a violet-coloured glow. If the pressure of the gas is reduced to about half a millimetre of mercury or less, the discharge changes again in appearance and stratification appears, the glow separating into distinct portions with dark spaces between.

Next the cathode or negative electrode there is a non-luminous space, especially noticeable, which is commonly referred to as Crookes' space, as these phenomena have been studied by him for many years. In order to explain some of the phenomena observed in highly exhausted vessels, Crookes¹ attributed them

¹ William Crookes was born in London on June 17th, 1832; after attending school at Chippenham he joined the Royal College of Chemistry in 1848, although his father had wished him to be an architect. In 1854 he obtained a post as Assistant in the Radcliffe Observatory, Oxford, and in 1855 he taught chemistry in Chester; the following year he came to London where he founded the *Chemical News* in 1859, of which he remained the sole editor until 1906. At the same time Crookes devoted himself to scientific research in this private laboratory, and in 1861 he discovered the new element thallium, by the aid of spectrum analysis. He made many investigations of the discharge of electricity through gases and of the scintillations produced by radioactive particles, and his discoveries were the starting-point for many important investigations in connection with the electron, positive rays, and related subjects. He held interesting and original views concerning a "fourth state" of matter (radiant matter), and his ideas on the nature and origin of the elements attracted much attention, although they must now be regarded as obsolete. Crookes was President of the British Association in 1898, and his presidential address at Bristol on the "Wheat Problem" created a stir in scientific and other circles; this is referred to in a later chapter on the Fixation of Nitrogen. He was elected to the Royal Society in 1863, and became Foreign Secretary (1908 to 1912) and later President (1913 to 1915); he was awarded the Royal, Davy and Copley medals of that society. Amongst many honours received by Crookes were a prize of 3000 francs awarded by the French Academy of Sciences in 1880, a knighthood in 1897, and the Order of Merit in 1910. Sir William Crookes died on April 4th, 1919. For many years he was interested in psychic phenomena and was President of the Society of Psychical Research.



William Brewster.

to new properties developed in the gas in consequence of the reduction in the number of molecules present. "The modern idea of the gaseous state is based on the supposition that a given space contains millions of millions of molecules in rapid movement in all directions, each having millions of encounters in a second. In such a case the length of the mean free path of the molecules is exceedingly small as compared with the dimensions of the vessel, and the properties which constitute the ordinary gaseous state of matter, which depend upon constant collisions, are observed. But by great rarefaction the free path is made so long that the hits in a given time may be disregarded in comparison to the misses, in which case the average molecule is allowed to obey its own motions or laws without interference ;

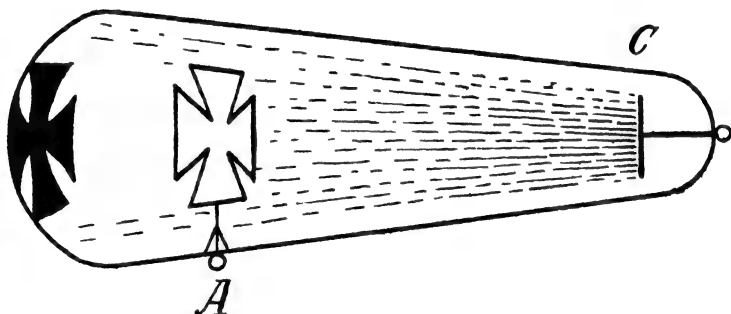


FIG. 40. PHOSPHORESCENCE AND SHADOW PRODUCED BY CATHODE RAYS

and if the mean free path is comparable to the dimensions of the vessel, the properties which constitute gaseity are reduced to a minimum, and the matter becomes exalted to an ultra-gaseous state, in which the very decided but hitherto masked properties now under investigation come into play." Matter then, according to Crookes, exists under the circumstances of a very high vacuum in what he regarded as a fourth state, which is neither solid, liquid, nor gaseous in the ordinary sense. This idea, although now known to be incorrect, helped to explain the facts that the radiation from the cathode appears to be material, that it travels in straight lines, and when it strikes on glass it produces phosphorescence. If a screen is interposed in the path of the rays, no phosphorescence is produced within the area of its shadow. If the cathode, instead of being flat, is made concave the rays thrown off from it may be brought to a focus, and in

this focus any solid object is heated intensely, and, if fusible, may be melted.

If the degree of exhaustion in the tube is increased beyond a certain point the discharge ultimately refuses to pass. Several other facts also require to be noted. For example, it was found by Lenard forty years ago that the emanation from the cathode when directed on to a very thin aluminium plate is capable of passing through it, at any rate it appeared to do so, as phosphorescence was excited on a glass surface a short distance from the opposite side. Such a fact was, however, difficult to reconcile with Crookes' hypothesis of electrified particles of the same dimensions as the molecules of ordinary matter. In 1895 the X-rays were discovered by Röntgen, and these X-rays, which are not material but consist of wave-like vibrations in the

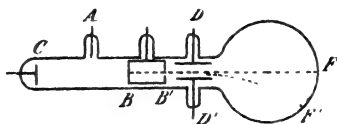


FIG. 41. J. J. THOMSON'S APPARATUS

hypothetical "æther," are produced by the cathode rays whenever they strike matter of any kind. The characteristic property of the X-rays is their power to penetrate more or less easily a great variety of substances opaque to ordinary light. It was observed by Röntgen almost immediately that when the hand is held in the path of these rays cast on a fluorescent screen, the shadow of the bones is darker than that of the flesh. Similarly these rays will pass through paper, wood, and metals of small atomic weight, such as aluminium, with little diminution, though they are completely stopped by a comparatively thin layer of a metal of high atomic weight, such as platinum, gold, or lead.

As the particles shot off from the cathode are material¹ and carry an electric charge, the path they follow may be regarded as the path of an electric current, and accordingly they are deflected by the action of a magnetic or electric field. Measurements and observations of the effects produced led Sir J. J.

¹ Recent developments in physics show definitely that electrons are also associated with wave-like properties. This discovery need not concern us here, but it must be emphasised that the study of the new wave mechanics of electrons is having a revolutionary influence on theoretical concepts in both physics and chemistry.

Thomson¹ to conclusions of the greatest importance as to the velocity and mass of these particles. The apparatus used is shown diagrammatically in Fig. 41. Here C is the cathode, A is the anode, and B B' are two metal plates each with a hole through the centre by which a pencil of cathode rays is conducted down the axis of the tube between the two parallel plates of aluminium, D D', which can be charged as required. A and B B' are connected to earth. When the discharge is passing the pencil of cathode rays falls on a zinc sulphide screen producing a spot of bright green light at F. If a difference of potential is established between the two plates D and D' the rays are bent down to some point F', and the radius of the circle into which they have been deflected can be calculated. The ratio of the mass of the cathode particle to the charge it carries can be calculated from the data thus obtained.

The cathode stream was found to consist not of atoms or molecules, but something much smaller which were at first spoken of merely as corpuscles, but the convenient term *electron*, introduced by Johnstone Stoney, was soon adopted, and has been generally used ever since. The word electron was originally employed to designate the atom of electricity or electrolytic unit which is carried by an atom of hydrogen in electrolysis (q.v.).

The mass of each of the cathode particles is about $\frac{1}{1836}$ of the mass of an atom of hydrogen, the smallest of known atoms. But the properties of the electron seem to have no connection with the nature of the gas through which the discharge takes place, nor with the material of the cathode itself. It is now known that similar electrons are emitted not only from ordinary

¹ Joseph John Thomson was born near Manchester on December 18th, 1856; he was educated at Owens College, Manchester, and at Trinity College, Cambridge. He was Second Wrangler and second Smith's Prizeman, for Mathematics, in 1880, and in 1883 was appointed Lecturer, at Trinity College. In 1884 Thomson became Cavendish Professor of Physics, at Cambridge, a post which he held until 1918; under his direction the Cavendish Laboratory became one of the world's most famous physics laboratories. On his retirement from the Cavendish Professorship, Sir Joseph John Thomson, he having been knighted in 1908, became Master of Trinity College, Cambridge, a position he still holds. He has been the recipient of many honours, at home and abroad; he was awarded the Royal, Hughes and Copley Medals of the Royal Society, of which he was President from 1916 to 1920. In 1902 he received the Order of Merit, and in 1906 the Nobel Prize for Physics. Sir Joseph Thomson's work has been concerned mainly with the discharge of electricity through gases: his work on the electron and on positive rays, mentioned in the text, has had a revolutionary influence in chemistry. Amongst other works, he has published *The Electron in Chemistry*, 1923.

atmospheric gases, but from the inert elements helium, argon, and the rest. Solids of many kinds, red-hot metals or metal surfaces illuminated by ultraviolet rays, as well as such oxides as lime and baryta, when heated also yield electrons. Radium and other radio-active substances emit them, and when derived from this source they are spoken of as β -rays. In fact electrons are to be found in all directions, and probably play an important part in many natural phenomena previously obscure.

There remains one important property of the electron to which no reference has so far been made, and that is its power of ionising gases. Under ordinary conditions air and other dry gas is an almost perfect non-conductor of electricity. But the residual gas in a vacuum tube through which a discharge is passing acquires conductivity, and at the same time becomes more or less luminous. Air in the presence of radium, as will be explained later, also acquires the power of conducting electricity. The ions thus produced are some of them positive and some negative; they are thought to be formed by the removal of a negative electron from a molecule of the gas which thus becomes positive, while the negative electron may attach itself to another molecule of the gas forming the negative ion. It seems also possible that they may be formed of fragments of molecules which have been broken up by collisions with the swiftly moving electrons. The latter gradually lose their energy in the process and ultimately lose their cathodic character, possibly entering into combination with some positive ion. The conductivity of the gas soon disappears if the supply of the ionising agent is not kept up, a consequence to be expected from the presence of both positive and negative atomic groups which naturally tend to recombine when they meet.

Thus far the origin and properties of the rays from the cathode have alone been described. But they are accompanied by rays of positive particles which are sometimes called "canal rays" from the manner in which they were first observed. If the cathode is perforated these particles pass through it, and move in straight lines in the opposite direction. The composition of these positive rays is much more complex than that of the cathode rays, for whereas the particles in the cathode rays are all of the same kind, there are in the positive rays many different kinds of particles. They are deflected by strong magnetic and electric fields, but less easily than the cathode rays, from which



J. J. Thomson.

it is inferred that their mass is greater than that of an electron. They appear to consist of positive ions, derived either from the gas or the electrodes, but they seem to start chiefly from the boundary of the Crookes' dark space. These rays were investigated by Sir J. J. Thomson,¹ who concluded that the particles constituting them have a mass never less than that of a hydrogen atom.

The following is a brief description of the apparatus used by Thomson :

A is a large bulb in which the anode is inserted on one side, the cathode C occupying the opposite neck of the bulb. In the diagram, for the sake of clearness, the tubes are not shown by which the gas is admitted into the bulb, nor the communication with the pump by which the contained gas is kept at the proper

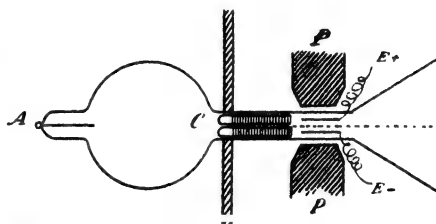


FIG. 42. J. J. THOMSON'S APPARATUS FOR STUDYING POSITIVE RAYS

low pressure. The cathode has in front an aluminium cap which fits on to a cylinder of soft iron with a hole bored along the axis. A very narrow copper tube, only about .1 mm. to .5 mm. in diameter, passes through this tube. The particles entering are therefore protected from magnetic forces till emerging from the copper tube, they pass between the poles of the electro-magnet PP, or the plates EE, by which an electric field can also be provided. The positive particles then strike on a photographic plate and there record a series of parabolas which depend on the gas or gases present in the tube.

It appears that each of the curves corresponds to a different atomic weight and that the ions are capable of carrying one, two, three or more unit charges. The method therefore can be used as the basis of a new method of analysis, and some very remarkable results have been obtained in connection with the weights of various elements. The most important of these is the proof that many elements, which were until recently believed to contain one type of atom only, really consist of a mixture of two

¹ See especially "The Bakerian Lecture for 1913" (*Proceedings Royal Society*, Vol. LXXXIX A, pp. 1-20).

or more atoms, having all properties except mass virtually identical. It will be seen later (chapter VII) that such different forms of the same element are called *isotopes*, and their existence was first suspected from a study of radioactivity.

Another strange result of the study of positive rays is that it appears possible to recognise temporary associations of atoms which are so unstable that they are unknown to the chemist. Thus when marsh gas CH_4 is used in the experimental tube fragments of the molecule CH_3 , CH_2 , CH and C appear to be able to record their presence on the photographic plate, although the life of each cannot be longer than a very small fraction of a second.

The discoveries which have thus resulted from a close study of the effects of the electric discharge naturally suggest hypotheses as to the constitution of atoms and the nature of chemical action. For the present it will be more convenient to postpone any discussion of this fascinating subject till the history of the elements and their known relations to one another has been laid before the reader.

The smallest positively charged particle detected by the positive ray method was one with a mass equal to that of the hydrogen atom: this was in fact an atom of hydrogen with a unit positive charge and the name *proton* (Greek, the first) was suggested for it by Sir Ernest (now Lord) Rutherford¹ at the meeting of the British Association in 1920. In spite of much search no particles of mass similar to that of the electron, that is about $\frac{1}{1800}$ th of the mass of a hydrogen atom, but carrying a positive charge had been detected either by positive ray or other methods, until 1932

¹ Ernest Rutherford (1st Baron Rutherford of Nelson) was born at Nelson, New Zealand, on August 30th, 1871, he studied at the University of New Zealand and later did research work at Cambridge. In 1898 he became Professor of Physics at McGill University, Montreal, and in 1907 was appointed Professor at the University of Manchester; in 1919 he succeeded Sir Joseph J. Thomson in the Cavendish Professorship of Physics at Cambridge. Rutherford was elected to the Fellowship of the Royal Society in 1903, and was awarded the Rumford and Copley Medals of that society, of which he was President from 1925 to 1930. He received the Nobel Prize for Chemistry in 1908, was knighted in 1908, awarded the Order of Merit in 1925, and raised to the Peerage, as Lord Rutherford, in 1931. His researches have dealt mainly with the properties and effects of radioactive substances; it was as a result of this work that he proposed the "nucleus" theory of the atom, and that the phenomena of the artificial disintegration of elements was discovered. In conjunction with Soddy he enunciated the revolutionary idea of radioactive transformation. Under Lord Rutherford's direction the great reputation of the Cavendish Laboratories at Cambridge has been maintained, and in it many important discoveries, some of which are considered in the text, have been made in recent years.

when Dr. C. D. Anderson, of California, obtained evidence for its existence in the course of experiments on the highly penetrating "cosmic rays" which appear to originate in the depths of space. Similar evidence was obtained shortly afterwards and independently by Dr. P. M. S. Blackett and Dr. E. P. Occhialini working in the Cavendish Laboratory at Cambridge; they found that in their passage through matter the cosmic rays produced both negatively charged electrons and the corresponding particles of small mass carrying an equal positive charge. These positive particles of light weight have been called *positrons*. Since their first discovery other methods for obtaining positrons have been found, and their existence can now be regarded as definitely established. There is still some doubt, however, whether the positron is like the electron in being a universal constituent of matter: the opinion most favoured at the present time is that they are not analogous in this respect. It is believed that a positron and an electron, with opposite electrical charges, are formed when penetrating radiation is absorbed by matter. According to this point of view the positron is merely a "hole in the æther" resulting from the removal of an electron!

CHAPTER VI

THE ELEMENTS OF THE CHEMIST

It is one of the characteristic features of modern physical science, which is not, like the ancient, content with observation of natural phenomena, but depends for progress on the results of experiment, to be perpetually in a state of flux. Its advance is analogous to the ascent of a mountain; the higher the traveller rises the broader is the prospect which becomes visible. He may now and then reach a plateau which tempts him to rest and look backward content for the time with the view, at the same time he knows full well that this resting-place is not the summit and that what he now sees will appear insignificant when a higher altitude is reached. Something of the same kind happens in the evolution of physical science. A theory is formed which for a time seems to provide a satisfactory explanation of all the facts under consideration. But before long some more accurate measurement or the observation of some neglected and

apparently trivial circumstance requires a revision of the accepted doctrine or its displacement by a new one.

These remarks apply specially to the case of the chemical elements. The word element has received many applications, and even at the present day in ordinary speech it is used sometimes in a poetical sense, with general allusion to air or water, or it simply means a constituent or ingredient in a mixture of things. Passing over any further reference to popular or ancient usage the word element received for the first time a definition with a scientific character from Robert Boyle in the seventeenth century. And this definition has been current among chemists since his day. An element, according to Boyle, is a substance which resists analysis. It consists of one kind of matter, and by no known process is it possible to extract from it more than one kind of stuff. It is only in the most recent times, namely, since the discovery of radium in 1902 and the related substances, that this definition, accepted as it has been for upwards of two hundred years, can no longer be applied without qualification to many substances which previously would have been included without hesitation under it. On the other hand, we have long since learned that several substances which formerly answered to the definition, having resisted the then known methods of analysis, such as lime, baryta, and the alkalis, are really compound bodies consisting of oxides of metals. But no real advance beyond a position of mere speculation could be accomplished until the phenomena of chemical combination were studied quantitatively and the laws of chemical combination were established. The law of definite proportions, the law of multiple proportions, and the law of reciprocal proportions were enunciated more or less clearly more than a hundred years ago, and all subsequent experiment has only served to establish them the more firmly. Then came in 1808 the Atomic Theory of John Dalton, which at once supplied an explanation of the observed facts. This theory assumes that each element consists of minute separate particles, all alike in size, weight, and chemical properties, and that when chemical combination takes place between any two or more elements to form a compound a definite and limited number of the particles of one kind are intimately associated with a definite and limited number of another kind.

Dalton himself began attempts to determine the relative

masses of the atoms conceived by his hypothesis, but the experimental methods available in his time did not admit of the attainment of accuracy. The subject, however, was pursued with improved methods and greater skill by a number of the most able chemists in the former half of the nineteenth century. The names of Berzelius, Dumas, Gay-Lussac, and Stas are prominent among the workers in that field.

The result of all their labours and that of a host of others was the establishment of a list of substances recognised as elements, in the sense already defined, together with the numbers which represent the relative masses of their atoms or what are called their atomic weights. The revision and criticism of these numbers has for many years past been undertaken by an International Committee of chemists, and a list is issued annually, under the authority of this committee, which represents the latest and best estimates of these important values. Till a few years ago hydrogen, as the lightest body known, was used as the standard for comparison, but after much discussion in the chemical world, which it is not necessary to follow in this place, it appeared more convenient to assume the atomic weight of oxygen to be represented exactly by the whole number 16, and to calculate all the rest accordingly. Hence the atomic weight of hydrogen is not now represented by the number 1.0, which would require the atomic weight of oxygen to be 15.88, but by the figure 1.0078 as given in the following table.

It ought to be understood that the atomic weights given in the list are not all equally trustworthy. Some, such as chlorine, potassium, silver, barium, represent a very high degree of accuracy, while others, for various reasons, such as possible presence of impurities or difficulties in manipulation of the compounds analysed, will probably suffer some slight revision in future years.

INTERNATIONAL ATOMIC WEIGHTS FOR 1934

Hydrogen . . .	1.0078	Oxygen . . .	16.000
Helium . . .	4.002	Fluorine . . .	19.00
Lithium . . .	6.94	Neon . . .	20.18
Beryllium . . .	9.02	Sodium . . .	23.00
Boron . . .	10.82	Magnesium . . .	24.32
Carbon . . .	12.00	Aluminium . . .	26.97
Nitrogen . . .	14.008	Silicon . . .	28.06

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Phosphorus . . .	31·02	Antimony . . .	121·76
Sulphur . . .	32·06	Tellurium ¹ . . .	127·61
Chlorine . . .	35·46	Iodine . . .	126·92
Argon ¹ . . .	39·94	Xenon . . .	131·3
Potassium . . .	39·10	Cæsium . . .	132·91
Calcium . . .	40·08	Barium . . .	137·36
Scandium . . .	45·1	Lanthanum . . .	138·92
Titanium . . .	47·9	Cerium . . .	140·13
Vanadium . . .	50·95	Praseodymium . . .	140·92
Chromium . . .	52·01	Neodymium . . .	144·27
Manganese . . .	54·93	Samarium . . .	150·43
Iron . . .	55·84	Europium . . .	152·0
Cobalt ¹ . . .	58·94	Gadolinium . . .	157·3
Nickel . . .	58·69	Terbium . . .	159·2
Copper . . .	63·57	Dysprosium . . .	162·46
Zinc . . .	65·37	Holmium . . .	163·5
Gallium . . .	69·72	Erbium . . .	167·64
Germanium . . .	72·6	Thulium . . .	169·4
Arsenic . . .	74·91	Ytterbium . . .	173·04
Selenium . . .	78·96	Lutecium . . .	175·0
Bromine . . .	79·92	Hafnium . . .	178·6
Krypton . . .	83·7	Tantalum . . .	181·4
Rubidium . . .	85·44	Tungsten . . .	184·0
Strontium . . .	87·63	Rhenium . . .	186·31
Yttrium . . .	88·92	Osmium . . .	191·5
Zirconium . . .	91·22	Iridium . . .	193·1
Columbium (Niobium) . . .	93·3	Platinum . . .	195·23
Molybdenum . . .	96·0	Gold . . .	197·2
Ruthenium . . .	101·7	Mercury . . .	200·61
Rhodium . . .	102·91	Thallium . . .	204·39
Palladium . . .	106·7	Lead . . .	207·22
Silver . . .	107·88	Bismuth . . .	209·0
Cadmium . . .	112·41	Radon . . .	222·0
Indium . . .	114·76	Radium . . .	225·97
Tin . . .	118·70	Thorium . . .	232·12
		Uranium . . .	238·14

The numbers which have been adopted in this table have all been selected so as to comply with certain rules long established and fully explained in the text-books of chemistry but outside the scope of this work.

¹ Placed out of order for reasons which will appear later.



L. Meni claff.

In addition to the eighty-five elements enumerated here, there are a number of others : illinium, of atomic weight about 147, has only been obtained in very small amounts ; polonium, actinium, and protoactinium, with atomic weights approximately 210, 230, and 234, respectively, are radio-active ; and in addition the existence of three other elements, masurium (approx. 100), alabamine (approx. 212), and virginium (approx. 224), has been claimed but not definitely proved. Including these uncertain elements the total number between hydrogen, the lightest, and uranium, the heaviest, is ninety-two.

As soon as a table such as the one just given could be drawn up a very important discovery was made. In 1863 it was observed by Mr. J. A. R. Newlands that in such a table, imperfect as it was at that time, the properties of the elements are related to their position in the series. Every eighth element in the list, starting from any point, exhibits a revival of the chief properties of the element from which counting is begun. Take, for example, the metal lithium as starting-point, the eighth element following it is sodium, and the eighth following is potassium, and these three elements form a natural family, the members of which are very like to one another in chemical properties, and show a gradation in physical properties. This discovery led to further investigation, and in the end the so-called periodic law of the elements was announced by the late Professor Mendeléeff in 1869.¹ This principle has been for the

¹ Dmitri Ivanovitsch Mendeléeff, was the fourteenth child of the Director of the College at Tobolsk, Siberia, where he was born on January 27th, 1834 (O.S.). He studied at the Pedagogic Institute in St. Petersburg, but on account of bad health he went to South Russia, where he taught science; he returned to St. Petersburg in 1856 and soon afterwards graduated and obtained a post at the University. Between 1859 and 1861 Mendeléeff studied in Paris and in Heidelberg, and in 1861 was appointed Professor of Chemistry in the Technological Institute at St. Petersburg. In 1866 he became Professor of General Chemistry at the University, but resigned his post in 1890 in consequence of a difference with the authorities. Three years later he was appointed to the office of Director of the Bureau of Weights and Measures, where he remained until his death on January 20th, 1907 (O.S.). Mendeléeff's name is indissolubly connected with the evolution and final establishment of the principle of periodicity among the elements; he was the first to foretell the properties of undiscovered elements, and to alter atomic weights in accordance with the requirements of the periodic table. He also carried out experimental researches on the constitution of solutions and the physical properties of gases, and gave considerable attention to the nature and origin of petroleum. Mendeléeff's famous manual entitled *Principles of Chemistry*, of which there have been several English editions and a new Russian edition issued to celebrate the centenary of

MENDELÉEFF'S PERIODIC TABLE, 1904.

Series.	Zero group.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
0	<i>x</i>	—	—	—	—	—	—	—	—
1	Hydrogen, H = 1.008	—	—	—	—	—	—	—	—
2	Helium, He = 4.0	Lithium, Li = 7.03	Beryllium, Be = 9.1	Boron, B = 11.0	Carbon, C = 12.0	Nitrogen, N = 14.04	Oxygen, O = 16.0	Fluorine, F = 19.0	—
3	Neon, Ne = 19.9	Sodium, Na = 23.05	Magnesium, Mg = 24.1	Aluminium, Al = 27.0	Silicon, Si = 28.4	Phosphorus, P = 31.0	Sulphur, S = 32.06	Chlorine, Cl = 35.45	—
4	Argon, Potassium, A = 38 K = 39.1	Calcium, Ca = 40.1	Scandium, Sc = 44.1	Titanium, Ti = 48.1	Vanadium, V = 51.4	Chromium, Cr = 52.1	Iron, Fe = 55.9	Manganese, Mn = 55.0	Nickel, Ni = 59 (Cu)
5	—	Copper, Cu = 63.6	Zinc, Zn = 65.4	Gallium, Ga = 70.0	Germanium, Ge = 72.3	Arsenic, As = 75.0	Selenium, Se = 79.0	Bromine, Br = 79.95	—
6	Krypton, Rubidium, Kr = 81.1 Rb = 85.4	Strontium, Sr = 87.6	Strontium, Sr = 87.6	Yttrium, Y = 89.0	Zirconium, Zr = 90.6	Niobium, Nb = 94.0	Molybdenum, Mo = 96.0	—	Ruthenium, Rhodium, Palladium, Ru = 101.7 Rh = 103.0 Pd = 106.5 (Ag)
7	—	Silver, Ag = 107.9	Cadmium, Cd = 112.4	Indium, In = 114.0	Tin, Sn = 119.0	Antimony, Sb = 120.0	Tellurium, Te = 127	Iodine, I = 127	—
8	Xenon, Cesium, Xe = 128 Cs = 132.9	Barium, Ba = 137.4	Barium, Ba = 137.4	Lanthanum, La = 139	Cerium, Ce = 140	—	—	—	—
9	—	—	—	—	—	—	—	—	—
10	—	—	—	Ytterbium, Yb = 173	—	Tantalum, Ta = 183.0	Tungsten, W = 184	—	Osmium, Iridium, Platinum, Os = 191 Ir = 193 Pt = 194.9 (Au)
11	—	Gold, Au = 197.2	Mercury, Hg = 200.0	Thallium, Tl = 204.1	Lead, Pb = 206.9	Bismuth, Bi = 208	—	—	—
12	—	—	Radium, Ra = 224	—	Thorium, Th = 232	—	Uranium, U = 239	—	—

last sixty years the most important guide in the study of inorganic chemistry.

The last version of his scheme of arrangement of the elements as left in 1904 by Mendeléeff, not long before his death, is shown in the preceding table ; it is, except for the addition of the more recently discovered elements and certain minor modifications, very much the same as that in use at the present day. One important change is the inclusion of a group of fourteen closely related elements from lanthanum (139.0) to lutecium (175.0), including cerium and ytterbium, and known as the "elements of the rare earths," together in Group III in a vertical arrangement ; the vacant spaces shown in the table between cerium and ytterbium may thus be regarded as non-existent. It is now known further that no elements are to be expected in Group VIII other than those shown. Attention should also be called to the spaces marked *x* and *y* ; the latter Mendeléeff imagined to be an analogue of helium with a density of about 0.2 and a molecular weight 0.4. He supposed that it might hereafter be identified with *coronium*, a hypothetical element existing in the sun's coronal atmosphere ; *x* is the "æther" of the physicist, for which Mendeléeff, disregarding conventional views, supposed a molecular or atomic structure. It was supposed also to be chemically inert and to have an extremely minute atomic weight. Neither of these is ever likely to be discovered, and in fact there is only one other element in the zero group, namely, radon (or radium emanation) preceding radium, the other spaces having no significance.

The spaces left vacant after hydrogen in Series 1 should be occupied, according to Mendeléeff, by elements, at the time unknown, having approximately the atomic weights 1.4, 1.8, 2.2, 2.6, 2.8, 3.0, and 3.4. There is good reason to believe that these elements never have existed nor ever will exist.

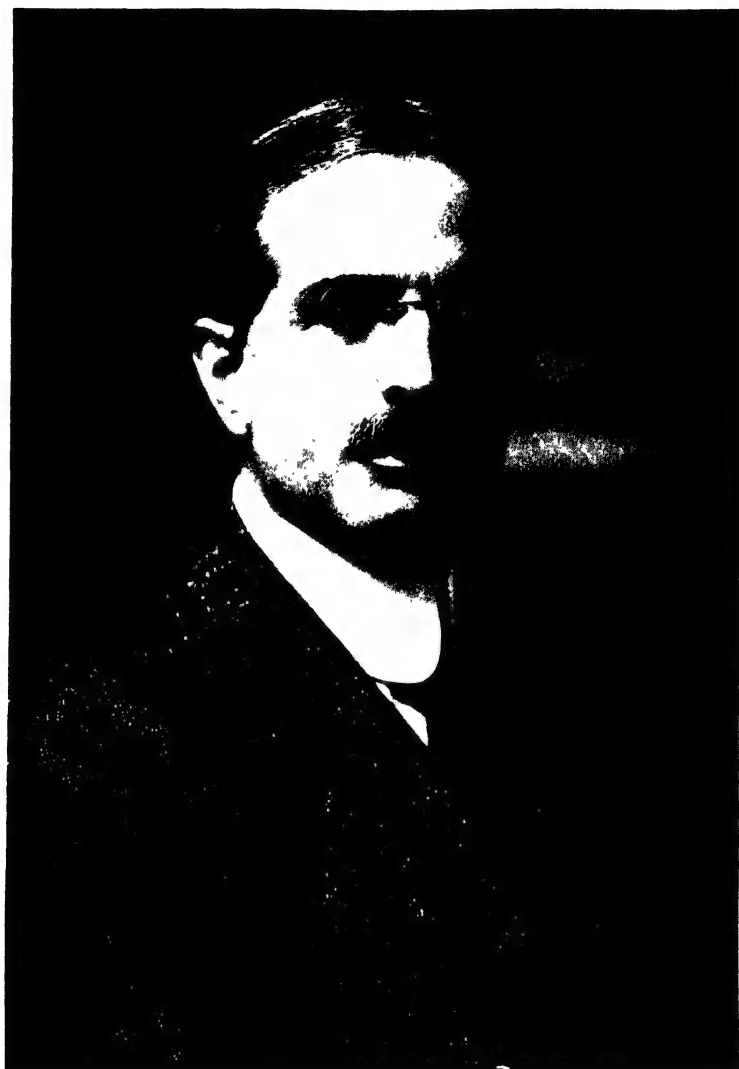
The important point of the arrangement of the elements in

his birth, had many original features and will always be a landmark in the history of chemistry. In 1882 the Royal Society conferred the Davy Medal on Mendeléeff, jointly with Lothar Meyer ; in 1890 he was elected a Foreign Member of the Royal Society, and awarded its Copley Medal in 1905. He received the Faraday Medal from the Chemical Society when delivering the Faraday Lecture in 1890. For further details concerning the life of Mendeléeff and the origin of the periodic classification, see the Memorial Lecture, by Sir William Tilden in the *Journal of the Chemical Society*, 1909, p. 2077.

the manner shown is not only the gradation of properties as one proceeds in a horizontal direction, but that all the elements falling into each vertical group have similar chemical and physical properties ; that is to say, there is a definite periodicity when the elements are arranged in order of increasing atomic weight. As is only to be expected small but regular variations are observed in passing down each group, from one element to the next of higher atomic weight. If there is a vacant space in the table, because the element which should occupy it has not been discovered, it should consequently be possible to forecast its properties from those of the elements above and below it in the same group, and at each side of it in the two adjacent groups : as will be seen shortly this is in fact what Mendeléeff did, and his prophecies were in several cases brilliantly confirmed by subsequent discoveries.

When the elements in each vertical group are examined in detail it is generally found that they can be conveniently divided into two sub-groups, the members of which resemble one another more closely than do those in the separate groups ; in Group I (see p. 112), for example, lithium, sodium, potassium, rubidium, and cæsium fall into one sub-group, and copper, silver, and gold into the other. The relationship between these two sets of elements is not very close, although some resemblances have been noted, but within each sub-group the similarities are very marked. In most modern forms of the periodic table the arrangement of the elements is such as bring out the existence of these and other sub-groups.

Periodicity is also clearly displayed when properties and atomic weights are plotted against each other in a system of rectangular co-ordinates so as to reveal a curve. The first scheme of this kind was published by Professor Lothar Meyer immediately after Mendeléeff's table in 1869. It displays the recurrence of maxima in the values of the atomic volumes when the elements are arranged consecutively in the order of their atomic weights. The physical properties of the elements have been the subject of much study since the time of Mendeléeff and Meyer, and it is now possible to show graphically that not only do atomic volumes wax and wane in following up the series, but other properties such as melting-points and coefficients of expansion follow the same order. The following diagram (Fig. 43) is taken from a paper in the *Journal of the American Chemical Society*



T. W. Richards

(July, 1915), by Professor T. W. Richards,¹ "Concerning the Compressibilities of the Elements and their Relations to other Properties." Here it is interesting to observe how closely the configurations of the several curves agree with one another, the maxima and minima in each case corresponding to the same atomic weight.

In the course of experiments on the specific heats of the elements at low temperatures between the boiling-points of liquid nitrogen and hydrogen, Sir James Dewar has observed that the mean atomic heats (at 50° Abs.) of the elements are a periodic function of the atomic weights. The atomic heat is to be understood as the product of multiplying the specific heat by the atomic weight, and at ordinary temperatures from the freezing to the boiling-point of water, the value of this product is almost uniformly 6.2 to 6.4 and periodicity has not been noticed.

At the temperature of only 50° absolute or 223° below centigrade zero the specific heats are very small, that of carbon in the form of diamond being only 0.0028 or $\frac{1}{357}$ of the specific heat of water. When these numbers are multiplied by the atomic weights the product is still of small numerical value. The figures for the atomic heats range from 0.03 for carbon to 6.82 for caesium. Doubtless the values in some cases will be slightly corrected by future experiment, but in the meantime the recognition of the periodic relation, that is, the rise and fall at regular intervals, is an interesting observation which brings the

¹ Theodore William Richards was born in Germanstown, Pennsylvania, on January 31st, 1868, his father being a well-known artist. After receiving a liberal education, in the widest sense, from his parents he went to Haverford College in 1882 and then to Harvard University, never having been to school. After graduation he would have taken up astronomy but for his bad sight, and so he devoted himself to chemistry and immediately became interested in atomic weights. Richards spent some time in Europe, and in 1889 he obtained an appointment at Harvard, where he remained for the rest of his life, first as assistant Professor, then as Erving Professor of Chemistry and finally, in addition, as Director of the Wolcott Gibbs Memorial Laboratory. His chief claim to fame rests on the great advances he made in the technique of the determination of atomic weights; in addition he carried out important work on the compressibility of the elements and on various thermochemical problems. Richards was a member of the American National Academy of Sciences, and of many European academies; he was awarded the Davy Medal of the Royal Society in 1910, the Faraday Medal of the Chemical Society in 1911, and the Willard Gibbs Medal in America in 1912. In 1915 he received the Nobel Prize for Chemistry. Richards died on April 2nd, 1928, whilst still occupying the Chair at Harvard. For an interesting account of Richards' life and work, see the Memorial Lecture by Sir Harold Hartley, published in the *Journal of the Chemical Society*, 1930, p. 1937.

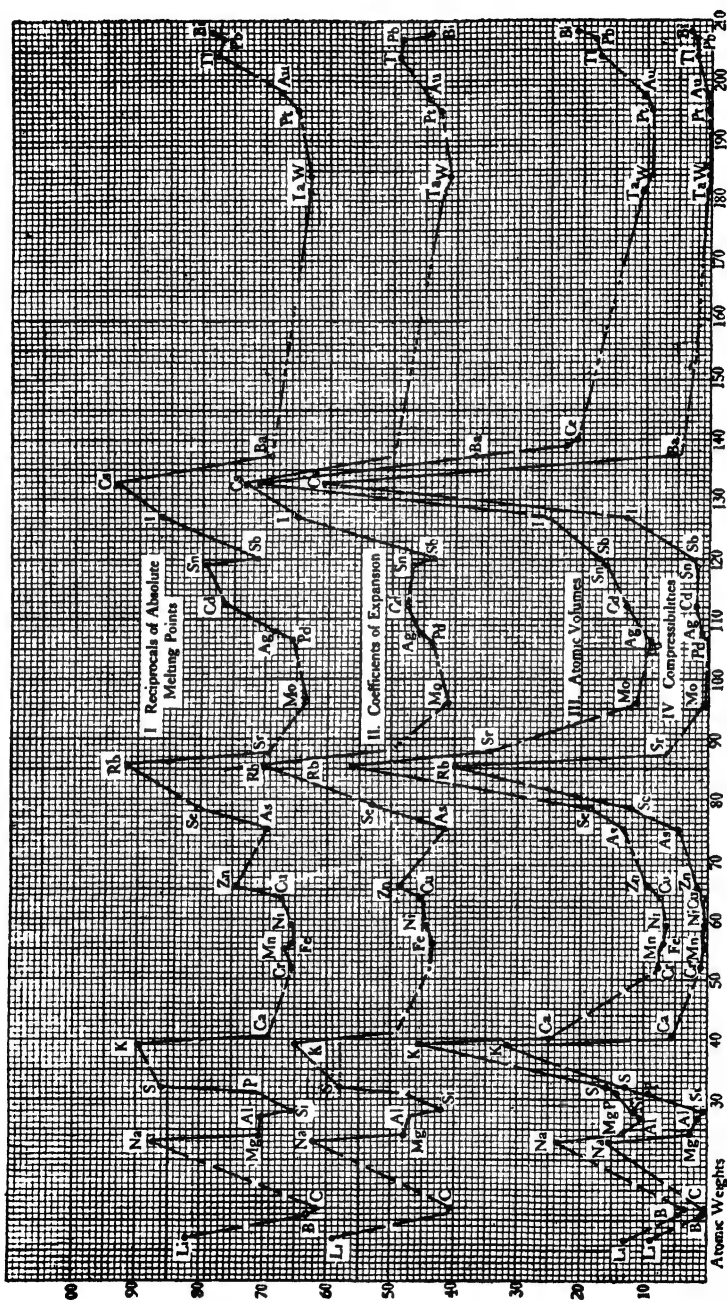


FIG. 43. PROPERTIES OF THIRTY-FIVE SOLID ELEMENTS.

After Prof. Richards (*J. Amer. Chem. Soc.*, July, 1915).

outstanding property of specific heat into the same category as the rest of the physical properties of the elements.

The diagram published in connection with Dewar's paper in the *Proceedings of the Royal Society*, vol. 89 (1913), p. 169, shows that the rise and fall of the curve follows very nearly the same course as the curve of atomic volumes originally pointed out by Lothar Meyer, and incorporated into the comprehensive diagram already given (page 116).

The importance of the periodic scheme, as arranged by Mendeléeff, deserves a little further notice in view of the influence it has had on the progress of theoretical chemistry. First of all it should be noticed that several of the elements now known were not known when the scheme was published. The table of elements first arranged by Mendeléeff in 1869 contained only sixty-three then recognised elements, the atomic weights being in many cases uncertain. But inasmuch as intervals too wide to be accounted for by mere experimental inexactitude occurred in several parts of the table, vacant spaces were left which suggested that substances existed somewhere in nature of which the chemist had not hitherto taken cognisance. And so it turned out. With most remarkable confidence in the trustworthiness of his scheme as indicating a law of nature, Mendeléeff proceeded to describe in detail the properties, chemical and physical, which would be exhibited by substances corresponding to the vacant places in the table, and in truly prophetic spirit to predict their discovery.

In 1871 the atomic weights represented approximately by the numbers 44, 70, and 72 were not known to belong to any existent element, but to the hypothetical elements expected to fill these places Mendeléeff gave the names ekaboron, ekaluminium, and ekasilicon.¹ In a footnote contained in his famous work on *The Principles of Chemistry*, the English translation of 1891 contains the following words :

"When in 1871 I wrote a paper on the application of the periodic law to the determination of the properties of yet undiscovered elements, I did not think I should live to see the verification of this consequence of the law, but such was to be the case. Three elements were described—ekaboron, ekaluminium, and ekasilicon—and now, after the lapse of twenty years, I have had the great pleasure of seeing them discovered

¹ Eka= Sanscrit meaning one.

and named after those three countries where the rare minerals containing them are found, and where they were discovered—Gallia, Scandinavia, and Germany.”

Between the elements zinc and arsenic then there were two unoccupied places, and the following are the chief properties which, according to the law, should appertain to them.

The following is the account given by Mendeléeff of the first of these :

“Zinc, which has an atomic weight 65, should be followed in the III group by an element with an atomic weight about 69. It will be in the same group as aluminium, and should consequently give R_2O_3 , $ROCl_3$, $R_2(SO_4)_3$, alums and like compounds analogous to those of aluminium. Its oxide should be more easily reducible to metal than alumina, just as zinc oxide is more easily reducible than magnesia. The oxide R_2O_3 should, like alumina, have feeble but clearly expressed basic properties. The metal reduced from its compounds should have a greater atomic volume than zinc, because in the fifth series, proceeding from zinc to bromine the volume increases. And as the volume of zinc is 9.2, and of arsenic 18, therefore that of our metal should be near to 12. This is also evident from the fact that the volume of aluminium is 11, and that of indium 14, and our metal is situated in the III group between aluminium and indium. If its volume is 11.5 and its atomic weight be about 69, then its density will be nearly 5.9. The fact of zinc being more volatile than magnesium gives reason for thinking that the metal in question will be more volatile than aluminium, and therefore for expecting its discovery by the aid of the spectroscope, etc.”

In 1875 Lecoq de Boisbaudran discovered, by means of the spectroscope, a new metal from the zinc blende in the Pyrenees, which he named *gallium*. It was found to yield an oxide R_2O_3 and an alum, that is a double sulphate with ammonium and potassium which crystallised in regular octahedrons. Its density was found to be 5.9, and its atomic weight 69.8. The metal was found to possess many of the properties of aluminium, being, however, much more fusible, just as zinc is more fusible than the next metal above it, namely magnesium.

In a similar way the properties of ekasilicon, foreseen by Mendeléeff in 1871, were recognised in the metal *germanium*, discovered by Clemens Winkler in 1886 in the peculiar silver

ore argyrodite. This element stands in Group IV of Mendeléeff's scheme, immediately below titanium, which follows silicon. The missing but expected element was described on the basis of a consideration of the properties of the known elements, silicon, zinc, tin, and arsenic, which in the table are placed at nearly equal distances from the vacant place.

It was expected to have an atomic weight nearly 72 with a higher oxide EsO_2 , and a lower oxide EsO , haloid compounds of the type EsCl_4 which would boil at about 90° . Its sulphide EsS_2 would resemble tin sulphide SnS_2 , and probably dissolve in ammonium sulphide and so forth. Germanium has an atomic weight 72.5, the metal melts at about 900°C . It forms a dioxide GeO_2 .

If germanium or its sulphide is heated in a stream of chlorine gas it forms a volatile liquid GeCl_4 , which boils at 86° , and is decomposed by water after the manner of stannic chloride. In fact the new element was found to possess just the properties to be expected of an element occupying a position intermediate between those of silicon and tin.

A similar correspondence was found to exist between Mendeléeff's ekabron and the metal *scandium* discovered by Nilson in 1879.

One other application of the periodic law may be mentioned, and that is the guidance it has afforded in correcting the atomic weights. The element beryllium had formerly the value 13.5 assigned to it. There is, however, no place in the periodic scheme for an element of this atomic weight with properties such as those exhibited by beryllium. A further investigation of its properties and determinations of its specific heat showed that the atomic weight was much lower, and the figure 9.1 entitles it to a place in the table in Group II, next above magnesium, with which it has considerable analogy. Other cases of a similar kind have led to correction which all experience tends to verify. Three elements only present outstanding difficulties. These are the elements argon, cobalt, and tellurium, which are placed in the list of elements one step too high in the consecutive order (see p. 110), so strong is the general conviction that their true places in the Mendeléeff scheme are those which have actually been assigned to them, notwithstanding the numerical discrepancy.

Justification for this strong conviction of the fundamental

correctness of the periodic classification came from the extremely important discovery made by the young physicist H.G.-J. Moseley,¹ when carrying out research in the laboratory of Professor (now Lord) Rutherford, in the University of Manchester, during 1913 and 1914. It has been already mentioned that the wave-lengths of X-rays depend on the nature of the material from which they are formed by the impact of cathode rays, and Moseley studied the frequencies, that is the reciprocal of the wave-lengths, of the characteristic X-rays produced by a number of elements. Each element actually causes the emission of several rays of different types, generally called K, L, M, etc., series, but it was found quite possible to compare the rays belonging to any one series; for the lighter elements Moseley used the K-series, whereas for the heavier ones the L-series of X-rays was found more convenient. It was observed that when considering a group of elements adjacent to one another in the periodic table, for example: titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper, the corresponding lines produced by the X-rays on a photographic plate were steadily displaced towards higher frequencies the heavier the element (Fig. 44). If the square roots of the X-ray frequencies were plotted on a graph against the atomic weights of the elements an irregular line was obtained, but if instead of the atomic weight the ordinal number of the element, representing its position in the periodic table, beginning with hydrogen as unity, was employed in the graph a straight line was obtained. The ordinal number of the element in the periodic table is known as its "atomic number" and the work of Moseley has shown it is this number, and not the atomic weight, which is the fundamental property of an element.

The concept of the atomic number not only provides the fundamental basis for the periodic classification, but it enables the so-called difficulties, to which reference has been made, to be overcome. For iron, cobalt, and nickel the X-ray frequencies are in the order given, and consequently this is the correct order of their atomic numbers and so represents their position in

¹ Henry Gwyn-Jeffrys Moseley was born in 1887 and educated at Trinity College, Oxford. He obtained a post at the University of Manchester under Rutherford in 1913, and subsequently went to Oxford. He was killed at Gallipoli on August 10th, 1915, but in his short life, so tragically ended, he made a contribution to science, referred to in the text, which will not soon be forgotten.

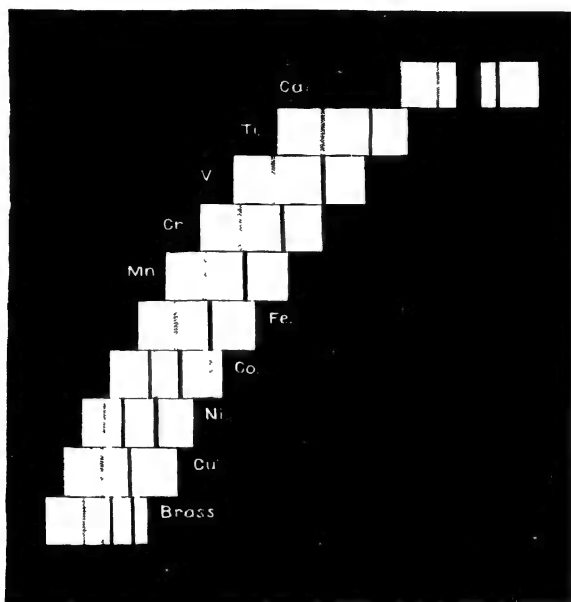


FIG. 11 —MOSELEY'S DIAGRAM OF CHARACTERISTIC X-RAYS OF SOME ADJACENT ELEMENTS IN THE PERIODIC TABLE

(By courtesy of the *Philosophical Magazine*.)

the periodic table, in spite of the discrepancy of their atomic weights. The same applies to tellurium and iodine, the atomic numbers of which have been found to be 52 and 53 respectively, corresponding with their true position in the Mendeléeff scheme, although the reverse of the order of their atomic weights. The study of the characteristic X-rays also clarified the situation concerning the group of rare-earth elements, for it permitted of a determination of their atomic numbers; it appeared quite definitely that in spite of the closeness of their atomic weights and their marked similarity of chemical properties there should be fourteen of these elements, from lanthanum to lutecium, inclusive, each occupying a definite position in the periodic table. On account of their similarity, however, all these elements are placed vertically in Group III.

The work on the relationship between atomic numbers and the characteristic X-rays may be regarded as the final vindication of Mendeléeff's ideas, and it is not surprising, therefore, that Lord Rutherford devoted a portion of his Mendeléeff Centenary Lecture to the Chemical Society (*Journal*, 1934, p. 635) to the subject. He said: "This discovery of Moseley represents an outstanding landmark in the history of our knowledge of the elements, for it fixed once for all the true order of the elements and showed that only 92 elements were possible from hydrogen 1 to the heaviest element uranium 92. It fixed at once also the number of elements possible in the group of rare earths. . . . Many of the anomalies in the Periodic Law at once disappeared when the atomic numbers of the elements were substituted for their atomic weights. . . . It became clear that the atomic weight of an element, though often running nearly parallel with the atomic number, was in a sense a secondary property. . . . Moseley's law not only fixed the ordinal number of the missing elements. . . . the use of the X-ray spectra provided a new and powerful method of analysis in the search for missing elements. The application of these ideas soon led to the discovery of hafnium 72, of masurium 43, and of rhenium 75."

The element argon has been mentioned, and we must now review as briefly as may be the dramatic story of its discovery.

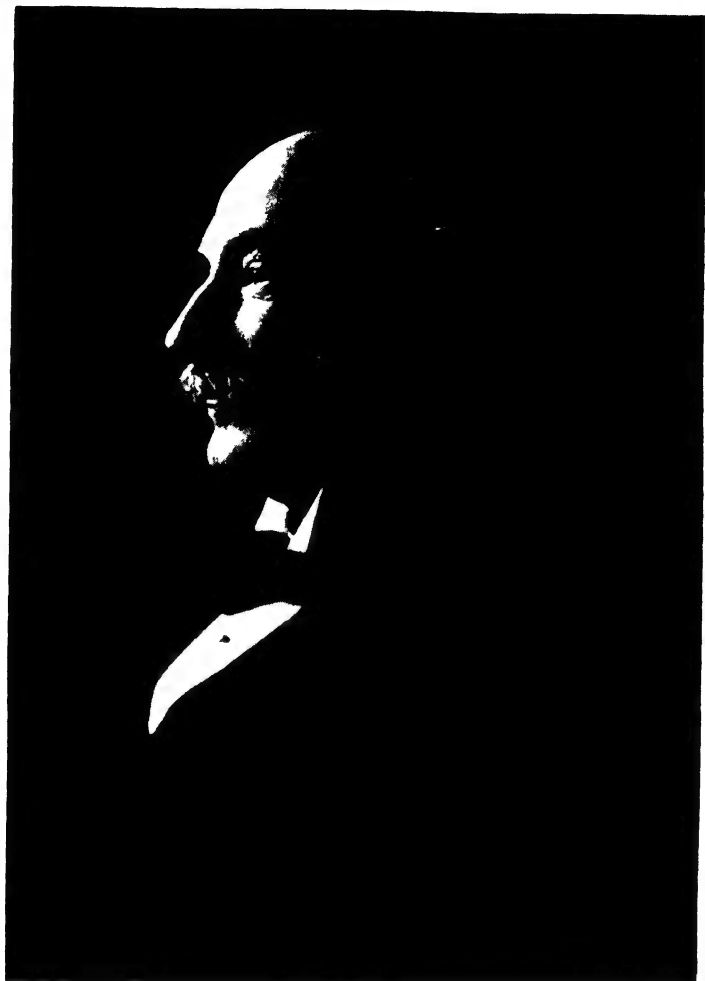
Previously to 1894 the existence of a group of elements destitute of all power to enter into chemical combination had not been foreseen by Mendeléeff or any of the chemists who had for years made a study of the periodic scheme. But for several

years Lord Rayleigh¹ had been engaged in a series of experiments, the object of which was to determine with the utmost possible accuracy, not only the relative densities, but the absolute densities, of the principal gases, that is, to compare their weights with that of an equal bulk of water. The method used was the same as that which had been employed by the French physicist Regnault many years before, and is in principle of the utmost simplicity. It consists in weighing the gas contained in a large glass globe attached to one arm of a balance, using as a counterpoise a similar globe of as nearly as possible the same size, so as to displace, with adjustments, exactly the same volume of air. The weight of the gas contained in the globe could thus be found, and, as the capacity of the globe had been previously determined, the volume of the gas was also known.

Having experimented on hydrogen and oxygen the case of nitrogen came to be considered, and an anomaly was soon discovered. It was found that when the nitrogen had been prepared from atmospheric air by removing the oxygen by any suitable agent, the gas proved to be heavier than the nitrogen made by chemical decomposition of ammonia or one of the oxides of nitrogen. Hence it might be supposed that the atmospheric nitrogen was too heavy on account of imperfect removal of oxygen, or the chemical nitrogen was too light in consequence of its contamination with gases lighter than pure nitrogen. It was proved by direct and laborious experiments that neither of these hypotheses could be adopted.

The following figures represent the weights of nitrogen, made

¹ The Rt. Hon. John William Strutt, Lord Rayleigh (3rd Baron), was born in 1842, he was Senior Wrangler and Smith's Prizeman (for Mathematics) at Cambridge in 1865. He devoted himself to the study of physical subjects, and carried out a large number of investigations in which the rare combination of high mathematical powers and experimental skill is manifest. Chemistry is indebted to Lord Rayleigh for his work on the densities of gases, begun about 1887, which culminated in the discovery of argon. He was elected a Fellow of the Royal Society in 1877, and was secretary from 1885 to 1896, and president from 1905 to 1908; he was awarded the Royal, Rumford and Copley Medals of this society and the Faraday Medal of the Chemical Society. Lord Rayleigh was one of the original members of the Order of Merit (1902), and received the Nobel Prize for Physics in 1904. He was Cavendish Professor of Physics at Cambridge from 1879 to 1884, Professor of Natural Philosophy in the Royal Institution (1887 to 1905) and Chancellor of the University of Cambridge. Lord Rayleigh died on June 30th, 1919, and was succeeded by his son, the Hon. R. J. Strutt, who discovered the active form of nitrogen whilst Professor of Physics at the Imperial College of Science, London.



St. Mary's Inf
Rearview

from different materials, with which the experimental globe was filled.¹

Nitrogen obtained from nitric oxide, NO	2·3001 grms.
„ „ „ nitrous oxide, N ₂ O	2·2990 „
„ „ „ ammonium nitrite, NH ₄ NO ₂	2·2987 „

Nitrogen was also made from air by first combining it with magnesium to form magnesium nitride, acting on this compound by water so as to produce ammonia and decomposing the ammonia by a hypochlorite. The nitrogen was finally purified by passing it over red-hot copper, and copper oxide.

The weight was then 2·29918 grams, and was therefore practically the same as above. Nitrogen obtained from atmospheric air by removing the oxygen by means of

Red-hot copper	weighed	2·3103 grams.
Red-hot iron	„	2·3100 „
Ferrous hydrate	„	2·3102 „

These figures correspond to the following weights per litre of the gas :

Chemical nitrogen	1·2505 grams.
Atmospheric nitrogen	1·2572 „

Further work led to the conclusion that atmospheric air contains an ingredient hitherto unnoticed by chemists. The announcement made at the Oxford meeting of the British Association in the summer of 1894 was received with a certain amount of incredulity by the chemical world, in view of the immense number of incontestably accurate analyses of air which had been made during the previous half-century. In these, however, the new ingredient, with its characteristic chemical inactivity, had always passed as nitrogen gas.

Lord Rayleigh had by this time secured the co-operation of Professor Ramsay, and the two investigators joined in laying before the Royal Society the results of their work. The interest excited was so great that a special meeting had to be held on January 31, 1895, in the theatre of the University of London, with Lord Kelvin, the president, in the chair.

In the paper then published the authors give reasons for suspecting a hitherto undiscovered constituent in air, and, as

¹ Rayleigh, *Proc. Royal Soc.*, 57 (1895), p. 267.

their statement contains so many interesting features, the following extracts from it will be welcomed by the reader. They say :

"When the discrepancy of weights was first encountered attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot copper oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity.

"At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules, N_2 , into detached atoms. In order to test this suggestion both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behaviour of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance their life would probably be short. On standing they might be expected to disappear, in partial analogy with ozone. With this idea in view, a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first. . . .

"The simplest explanation in many respects was to admit the existence of a second ingredient in air, from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, $\frac{1}{2}$ per cent only by volume would be needed ; or if the density were but half as much again as that of nitrogen, then 1 per cent would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected. . . .

"And here the question forced itself upon us as to what really was the evidence in favour of the prevalent doctrine that

the inert residue from air, after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

"The identification of 'phlogisticated' air¹ with the constituent of nitric acid is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U tube.

"Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And, what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the nature of the phlogisticated part of our atmosphere, than that it is not diminished by lime-water, caustic alkalies, or nitrous air; that it is unfit to support fire, or maintain life in animals; and that its specific gravity is not much less than that of common air: so that, though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and, consequently, though it was reasonable to suppose that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it might fairly be doubted whether the whole is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature from the rest which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet, as some remained unabsorbed, it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common

¹ That is deprived of oxygen. Phlogisticated air is in modern language nitrogen; dephlogisticated air was afterwards named oxygen by Lavoisier.

air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompose as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark till no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.'"¹

The authors repeated this experiment of Cavendish with the advantage of modern apparatus, and they found that on sparking air with added oxygen in the presence of potash the residue which remained unabsorbable was in proportion to the amount of air operated on. An examination of this residue with the spectroscope showed that it was not nitrogen, but had a spectrum of its own; it was a hitherto unidentified gaseous element to which the name *argon*² was given.

To prepare argon on a large scale air is freed from oxygen by means of red-hot copper. It is then dried by means of soda lime and phosphoric oxide, and the nitrogen is absorbed by passage through a tube packed with magnesium turnings heated to bright redness. The residual gas is then made to circulate through an apparatus containing hot copper, copper oxide, soda lime, and magnesium, by which the last traces of impurities are removed.³

Argon is a colourless gas 19.95 times heavier than hydrogen, and therefore nearly 1.4 times heavier than air. It is soluble in water to about the same small extent as oxygen, that is, approximately 4 volumes in 100 of water at common temperatures.

All attempts to induce argon to enter into chemical combination have proved abortive. Most drastic treatment was applied and a great variety of reagents used, but argon remains

¹ Cavendish's "Experiments on Air," *Philosophical Transactions of the Royal Soc.*, 1785.

² The name is derived from the Greek (*ἀν* privative, *ἔργον* work), in reference to its chemical inactivity.

³ Details are described in the original paper entitled "Argon, a New Constituent of the Atmosphere," *Proc. Royal Soc.*, 57 (1895), p. 265.

in all these circumstances unaltered. No substance of this kind having been previously known it will be understood that the ingenuity of the discoverers and the efforts of many other chemists were employed to settle this point conclusively.

In the paper of which an account has just been given the discoverers assume, provisionally, that the gas they had succeeded in isolating was a single substance and not a mixture of gases.

The density of argon being 19.95 the law of Avogadro indicates that its molecular weight is 39.9. The molecule is believed to consist of one atom only, and this is designated by the symbol A.

At the anniversary meeting of the Chemical Society on March 27th, 1895, a fresh surprise awaited the assembled chemists. The discovery of a new element similar in character to argon was announced by Professor Ramsay. In seeking a clue to compounds of argon he was led to repeat experiments of Hillebrand on the rare mineral clèvite, which, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen.

This gas proved to contain very little nitrogen with traces of argon, but examination with the spectroscope showed that the most prominent line was a brilliant yellow one very close to the two lines of sodium, D_1 and D_2 , but only known up to this time as belonging to a constituent of the sun's chromosphere and designated D_3 . This line had been attributed by Professors Janssen and Lockyer, thirty years previously, to a hypothetical solar element which was named by them *helium*.

Clèvite, the mineral originally used, is a variety of uraninite, and contains beside uranium and lead a considerable quantity of the rare earths. The significance of the association of helium with uranium and lead will be referred to on a later page.

Helium has been found to be a constituent of a large number of minerals, but it is especially found in connection with compounds of uranium, thorium, and the rare earths. It is a colourless inert gas like argon, but very much lighter, being, in fact, with the exception of hydrogen, the lightest gas known. Its density is 2.0, and hence its molecular and atomic weight is 4.0. It was found to be very sparingly soluble in water, one volume of the gas being soluble in between 130 and 140 volumes of water, at atmospheric temperatures. This low degree of solubility indicated a probably low boiling-point. The subsequent history of helium confirmed this conjecture, for it was not till

1908 that helium was reduced to the liquid state by Professor Kamerlingh-Onnes of Leiden. The boiling-point was found to be about 4.5° absolute or 268° to 269° C. below 0° C. This result, by which the last of the known gases was made to change its state, was only accomplished by pressure with the aid of liquid hydrogen as a cooling agent (see p. 72).

These two remarkable elements helium and argon presented a difficult problem as to their position in relation to the rest of the chemically active elements.

On reviewing Mendeléeff's periodic scheme of the elements it is noticeable that, if we regard for the moment only the elements known prior to the discovery of helium and argon, the valency or combining capacity of the atoms in Group I is represented by unity. These elements are univalent. The same is the characteristic valency of the halogens, fluorine, chlorine, bromine, and iodine, which stand, along with manganese, somewhat doubtfully in the Group VII. If then, following the order from left to right, it is found that the valency steadily increases as shown below, it appears that if a column is provided to the left of Group I any elements finding a position therein would have a valency one unit less than 1, i.e., 0.

Valency	0	1	2	3	4	5 or 3	6 or 2	7 or 1
	He 4	Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0
		Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5
	A 39.9	K 39.1	Ca 40.1	Sc 45.1	Ti 47.9	V 51.0	Cr 52.0	

The differences between the first and second lines are pretty constantly equal to very nearly 16 units, thus $23 - 6.9 = 16.1$, etc. The differences between the second and third lines are at first about 16, but increase in passing from left to right. If helium and argon are introduced into such a table it is at once observed that there is an interval between them which would apparently require an element having an atomic weight 16 units greater than that of helium, or approximately 20. The question then arises does such an element exist?

This question Ramsay set to work to investigate in conjunction with Dr. M. W. Travers. Many fruitless experiments were undertaken on the gases obtained from minerals and in attempts to separate helium and argon into two elements by means of diffusion

The gases were obtained from mineral waters, such as the hot springs at Bath, and the waters of Cauterets in the Pyrenees in which argon and helium had been found. The production of liquid air on a large scale provided the material from which the first success was obtained ; and, after allowing about a litre of it to evaporate away, the last portions were found to contain a gas having about twice the density of argon to which the name *Krypton* (Gr. hidden) was given. Very shortly afterwards, by liquefying a large quantity of "argon," obtained from atmospheric air, and in a similar manner allowing the liquid to evaporate, the successive fractions yielded two other gases. The one lighter than argon fitted the place already prepared for it in the periodic table ; it was called *Neon* (the new one). The other had a density of 64, and was found in small quantity in the least volatile portions of the liquid, and was named *Xenon* (the stranger). The complete story of these wonderful researches by Lord Rayleigh and Professor Ramsay deserves to be read in the original papers by every serious student of chemistry. The details of the countless experiments, the ingenuity in devising apparatus, the skill involved in its manipulation, and the knowledge which could turn to account so many physical facts and methods have never been surpassed and perhaps not equalled in the history of physical science.

There is one other point worthy of notice. The periodic scheme is justified completely, notwithstanding necessary qualifications, by the results of this work, for by its use discoveries have been made which, without such a guide, would probably have remained unsuspected for ever.

The new elements are as follows, and they will be found in the table (p. 112) in their several positions.

Name.	Symbol.	Atomic or molecular weight.
Helium	.. He	4.00
Neon Ne	20.18
Argon	.. A	39.94
Krypton	.. Kr	83.7
Xenon	.. Xe	131.3

} Most
recent
estimates.

To these, for it belongs to the same group of inactive gases, must now be added the emanation from radium, called *radon* ; it is given the symbol Rn and has an atomic weight of about 222.

It may be mentioned in conclusion that three of these gases, discovered as a result of a purely scientific investigation into

discrepancies in gas density measurements, have now become of industrial importance. Helium, obtained from natural gas in North America, because of its lightness and non-inflammability has been used for filling airships ; neon and argon, extracted from the air, are contained in glowing electric signs and in " gas-filled " or " half-watt " electric lamps, respectively.

CHAPTER VII

DISCOVERY AND PROPERTIES OF RADIUM

WHILE all this work was going on in England researches were proceeding in France which were destined to lead to other surprising discoveries. The X-rays had been discovered by Professor Röntgen of Würzburg in the autumn of 1895, and early in 1896 Henri Becquerel, Professor of Physics in the Museum of Natural History in Paris, set to work to examine the radiations emitted by phosphorescent bodies of all kinds, in the expectation that the luminous rays might be accompanied by invisible but penetrating radiation, identical with or similar to the Röntgen rays. Observations on the radiating properties of the salts of uranium led him to the discovery that these substances possess the property of affecting a photographic plate. In the first experiments the uranium compound was exposed to the rays of the sun while the sensitised plate was protected by black paper and a sheet of metallic aluminium.

A few days later he discovered, almost by accident, that exposure of the whole to light was unnecessary, and that if the crystal was kept attached to the plate long enough a very strong impression was obtained in the dark. It thus appeared that the phenomenon could not be attributed to luminous radiations emitted by reason of phosphorescence, since at the end of one-hundredth of a second phosphorescence becomes so feeble as to be imperceptible. It appeared then that the photographic action produced by an uranium compound was a phenomenon of a completely new order. In order to ascertain whether it was due to energy stored up in the crystal and that the effect would disappear or diminish with time, some years would have been

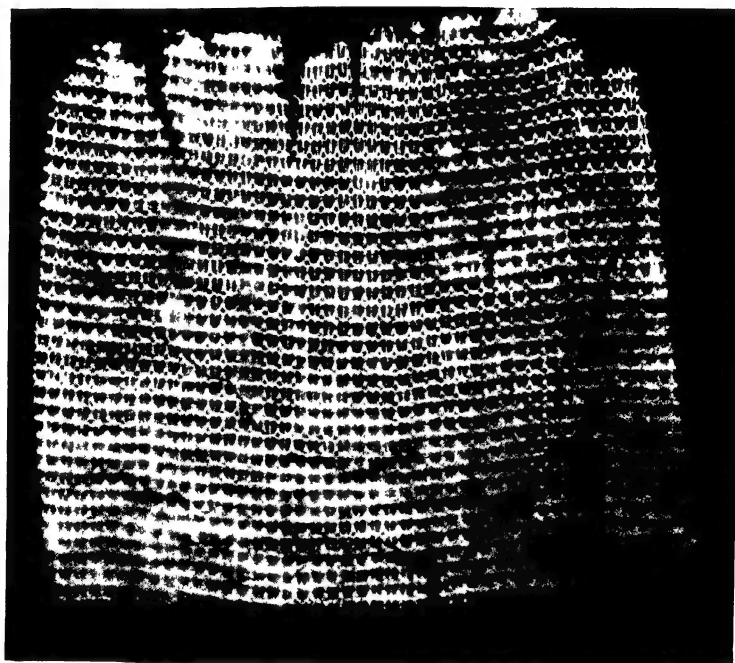


FIG. 45 —EFFECT OF GAS-MANTLE ON A PHOTOGRAPHIC PLATE IN THE DARK,
DUE TO RADIO-ACTIVITY OF THORIUM

(From Soddy's "Interpretation of the Atom", by courtesy of Messrs. John Murray)

necessary. Fortunately Becquerel discovered almost immediately after the photographic experiments just mentioned, that the new radiation had the property of rendering the surrounding medium an electrical conductor, and consequently of discharging electrified bodies when brought near them. He used a gold leaf electroscope, of which a common form is shown in the figure. A couple of strips of gold leaf are attached to the end of a brass rod having a brass disc at the top. The leaves must be protected from draughts of air, etc., and they are therefore suspended inside a glass case, the rod being electrically insulated by means of ebonite or some good non-conductor. When the plate is electrified the gold leaves receive part of the charge, and both being alike either positive or negative are repelled by each other and so diverge. Under ordinary circumstances in air the charge slowly leaks away and the leaves collapse again. In the presence of a radio-active substance the leaves of the electroscope collapse more rapidly, at a rate which can be measured by having a scale on the glass case.

Like the X-rays those discovered by Becquerel travel in straight lines and are capable of traversing wood, paper, and the less dense metals such as aluminium. The radio-activity of a uranium compound is, however, tested more conveniently by the use of the electroscope, and it was by the systematic use of this instrument that Madame Curie,¹ assisted by her husband,

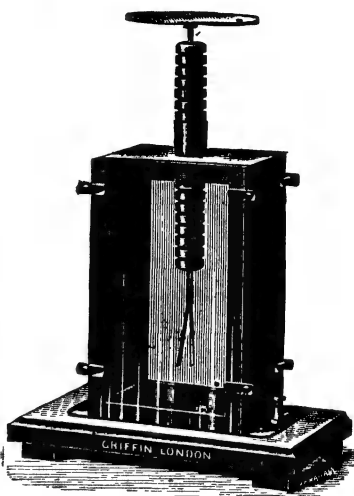


FIG. 46. GOLD LEAF ELECTROSCOPE

¹ Marie Curie, née Marie Skłodowska, was born at Warsaw on November 7th, 1867; she was first educated in her native city, but as a result of being involved in a students' political movement she found it advisable to leave, and after going to Cracow she went to Paris to study at the Sorbonne. In 1895 she graduated, and in the same year married Professor Pierre Curie with whom she worked on the radio-active properties of minerals. It was during the course of this work that radium was discovered and its atomic weight determined; a full account was given in Madame Curie's thesis for the degree of Docteur ès Sciences, presented to the University of Paris in 1903. A full translation was published in the *Chemical News* of that year. Professor Curie was killed in a street

the late Professor Curie, was led to the discovery of radium. By the examination of a large number of uranium and thorium minerals it was found that the electrical conductivity of the air induced by the rays from an uranium compound varies directly with the amount of this element present in the mineral. All uranium compounds are active, and the metal itself more so than any of its salts, except pitchblende or uraninite, U_3O_8 , and native chalcocite (copper uranyl-phosphate). The latter substance, when prepared artificially, was found to be less active than the metal. Hence it appeared that the natural minerals contained a substance far more active than uranium. Thorium compounds were found to be active, the action of some of them being actually more pronounced than that of uranium.

A specimen of pitchblende possessing $2\frac{1}{2}$ times the activity of uranium was examined chemically with the object of isolating the radio-active substance. The mineral dissolved in acids was brought into contact with sulphuretted hydrogen, and it was found that the uranium and thorium remaining in solution, the active substance was precipitated with the sulphides insoluble in ammonium sulphide. After separating these in the usual manner it was found that the active substance remained with the bismuth. An extremely active substance was also obtained from pitchblende by sublimation, and when the sulphides were heated in a vacuum at 700° a sublimate was obtained possessing an activity 400 times that of uranium. By further treatment a very active substance was obtained to which the name *polonium* was given in honour of Madame Curie's native country.

The chemical examination of the uraniferous minerals studied by the Curies proceeded nearly on the lines of the ordinary method of qualitative analysis. In the sulphides obtained polonium had been recognised, but another very active substance was found to be associated with the barium also present. Barium is easily separated from solution by sulphuric acid, which causes it to be thrown down as a white insoluble precipitate consisting of the sulphate. This sulphate was accompanied by

accident in Paris in 1906, and on his death his widow succeeded him as Professor of Physics; she was also made head of the Radium Institute established in her honour. Madame Curie was unique in having twice received a Nobel Prize: in 1903 she shared the Prize for Physics with her husband and Becquerel, and in 1911 was awarded the Prize for Chemistry. She died on July 4th, 1934. The Curie Memorial Lecture was delivered before the Chemical Society of London by Dr. A. S. Russell and published in its *Journal*, 1935, p. 654.



Mr. Curie

the active substance. The sulphate was converted into the chloride, and it was then found that a partial separation of the inactive barium from the attendant active substance could be effected by taking advantage of the greater degree of solubility of the barium chloride in water, alcohol, or hydrochloric acid. Ultimately it was found that separation was more easily effected by fractional crystallisation of the bromides. The new substance was the bromide of the previously unknown element about to become so famous under the name of *radium*.

According to Professor Rutherford the amount of radium present in a mineral is uniformly about 3·4 parts for 10,000,000 parts of the uranium present. Consequently there is only 1 gram of radium to roughly 3 tons of uranium.

The process of extracting radium on a large scale from pitchblende residues which contain barium and radium together is extremely expensive and laborious. A complete account of the operations required as well as of the properties of radium examined and recorded up to that date is provided in the Thesis presented by Madame Curie to the Faculty of Sciences of the University of Paris in 1903. This is printed *in extenso* in the *Annales de Chimie et de Physique*.

The nature of the process has already been sufficiently stated. The first supplies of material were given by the Austrian Government from the residues left after the extraction of uranium from the pitchblende in the State mine at Joachimsthal, now in Czecho-Slovakia. This was at one time the chief source of radium, but uranium minerals have been since discovered in Colorado, in Saxony and especially in the Belgian Congo, so that the once famous St. Joachimsthal mines are now of minor importance. Pitchblende has also been found in Cornwall, but the amounts are relatively small.

Radium bromide is still very costly, the price being about £7 per milligram at the present time. The enquirer must therefore not expect to see anything more than what appears as a contemptible little grain of salt at the bottom of a small glass tube perhaps an inch long. There is, however, a reason other than the cost, which would preclude the exhibition of any large quantity such as a quarter of a pound if at any time so much should become available. Its physiological effects are so powerful that any large quantity is dangerous to handle.

A small tube containing only a few milligrams was long ago

found to produce a sore on the body if carried in the pocket. It is this caustic effect of the radiations from radium which is being used experimentally for medical purposes on cancers and other malignant growths in the human tissues.

A specimen of radium then looks like a few grains of common salt, which, however, is slightly luminous, and therefore visible in the dark. But one of its most striking properties is the power it possesses of exciting phosphorescence in other substances brought near it. Thus all diamonds give out light of various tints and intensity in the presence of radium, and a certain variety of blende (native zinc sulphide) lights up brilliantly. This property is utilised in the manufacture of the so-called luminous paint for watch dials. On examining the light given forth by the zinc sulphide by means of a magnifying glass it was observed to be due to brilliant separate flashes which are more numerous as the radium is nearer to the screen and so less numerous as it is further away, that the sparks, which appear like stars on a black sky, may be counted.

This effect was discovered by Sir William Crookes, who has arranged a simple apparatus called the spinthariscopes (Gr. *σπινθαρῖς*, a spark) for observing it. This consists of a tube about two inches long, having a zinc sulphide screen at one end with a small surface coated with a radium salt near it. At the other end is a low-power lens through which the sparks can be seen.

Contact with a radium salt is followed in some cases with remarkable changes of colour. Sir William Crookes possessed a diamond which, having been embedded in radium bromide for some months, had assumed an olive-green colour though unchanged in other respects. This colour could not be removed by boiling the stone in acids or other chemical agents. The glass tubes in which radium salts have been kept always become discoloured, generally assuming pretty rapidly a purplish tint. Sir William Crookes has also shown that the diamond may acquire and retain the property of radio-activity for a long period.

Another very remarkable fact about radium (discovered by P. Curie and Laborde in 1903) is that a mass of the salt is always at a temperature several degrees above that of the surrounding atmosphere. Obviously the exact difference will depend upon circumstances, but this spontaneous liberation of energy was

made the subject of many later experiments, and among other facts it was found that the rate of emission depended on the age of the specimen. The quantitative estimation of the heating effect by Rutherford and Barnes in 1904 led to the result that one gram of radium bromide gives out 110 gram calories per hour. This discovery has had the important effect of rendering invalid calculations of the age of the earth, such as those of Lord Kelvin, based on the rate of cooling of the earth's crust. The heat developed continuously by radium counteracts the effect of cooling influences, and Rutherford calculated that "the presence of 4.6×10^{-14} gram of radium per gram uniformly distributed throughout the volume of the earth would produce as much heat as that lost by conduction to the surface. In other words, with such a distribution of radium, the temperature gradient of the earth would remain constant."

The element radium was obtained in the metallic state in 1910 by Madame Curie and M. Debierne. It is a white metal which melts at about $700^{\circ}\text{C}.$, and which dissolves in water, decomposing it and forming the alkaline hydroxide, hydrogen gas being given off. The salts of radium are very similar to those of barium, and it agrees in general properties, valency, etc., with the metals of the alkaline earths, and is consequently placed in the periodic table below barium. But while the other members of the same series are destitute of radio-active properties the activity of radium as measured by the electroscope is about 2,000,000 times that of uranium.

The atomic weight of radium has been the subject of much careful experiment. The conditions necessary to ensure the utmost possible accuracy in such determinations, and the chief considerations involved have been so admirably exposed in the paper by Sir William Ramsay and Dr. R. Whytlaw-Gray on "The Atomic Weight of Radium," in the Proceedings of the Royal Society for 1912, p. 270, that we cannot do better than quote the greater part of the introductory portions of this paper. It not only gives the history of the important question as to the atomic weight of radium, but it affords very instructive information as to the procedure in work of this kind in general.

"The essentials in determining the correct equivalent of an element are :

"(1) A pure compound of the element and sufficient evidence of purity.

"(2) An advantageous transformation in which the weight of the element or elements combined with the one of which the equivalent is to be determined is as large as possible.

"(3) If possible no transference, and no operation which necessitates the use of reagents which can convey into the solution matter which may be absorbed.

"(4) A quantity sufficient in amount to make it possible with the balance at disposal to determine its weight to, at least, 1 part in 20,000.

"(5) Resistant vessels which will not themselves give up any material to the substance and so make its purification difficult.

"Determinations of the equivalent of radium have been made by Madame Curie, by Sir Edward Thorpe, and by O. Hönschmid. Madame Curie's first determination, made in 1902, may be taken as avowedly only a rough approximation. Using 90 mgrm. of chloride she found the atomic weight to be 225, assuming, no doubt with justice, that radium is a diad. Her second determination employed the same method, viz., precipitation and weighing of silver chloride from a known weight of anhydrous radium chloride. Madame Curie, in her earlier work, proceeded to the ultimate atomic weight progressively, raising the number from 140 to 146, then 174, then greater than 220, and in 1902 to 223.3; finally, with 90 mgrm., she obtained the figures 225.5, 226.0, and 224.2; mean 225.2, which she regarded as accurate within a unit.

"The method of crystallisation described in her later paper is merely indicated. . . . The samples were tested spectroscopically for barium. . . . The amount taken was about 0.40 grm. After deducting the weight of the filter ash the figures 226.62, 226.31, and 226.42 were obtained, the values for $Ag=107.93$ and $Cl=35.45$ having been taken. Substituting 107.88 and 35.46 the figures are less by 0.09 or 226.53, 226.22, and 226.33; the mean of these is 226.36. . . .

"In his Bakerian Lecture for 1907, Sir Edward Thorpe described experiments on the equivalent of radium. His raw material, placed by the courtesy of the Austrian Government at the disposal of the Royal Society, was 'about 500 kgrm.', or, say, half a ton of pitchblende residues from Joachimsthal. These residues were delivered by the Austrian Government to M. Armet de Lisle in Paris for preliminary extraction. . . .

"Thorpe received from Paris 413 grams of mixed chlorides of

barium and radium, the radio-activity of which was 560 times that of uranium. . . .

"The method of separation of radium and barium followed by Thorpe was substantially the same as that adopted by Madame Curie; 9400 recrystallisations of the chlorides were carried out, towards the end in silica vessels. . . .

"The analytical process was also identical with that employed by Madame Curie, namely, precipitation of silver chloride from the dissolved radium chloride acidified with nitric acid, subsidence, washing with distilled water six times, drying at 160°, and weighing on an assay balance sensitive to 0.1 mgrm. . . .

"The results of Thorpe's determinations are:

I. 226.7

II. 225.6

III. 227.6

"A new set of determinations has been made by Hönigschmid (1911) in which quantities somewhat exceeding 1 gram were used. The method of purification was again that employed by Madame Curie and Thorpe, viz., repeated crystallisation of the chlorides from hydrochloric acid and precipitation of the aqueous solution of the salt with alcohol. The equivalent was not altered after 50 such crystallisations and 13 precipitations with alcohol, and that material was regarded as pure, and employed in the final determinations. The method, too, was the same as that described, but in two cases the chloride of silver was reduced and the weight of the silver ascertained. The mean result, taking $\text{Cl}=35.46$ and $\text{Ag}=107.88$, was 225.95. The extremes in seven determinations were 225.92 and 225.97.

"Whilst these researches show the approximate atomic weight of radium it cannot be said that the results must be accepted as final, for they are lacking in several of the conditions stated at the beginning of this paper. There is the possibility of contamination of the solutions with the reagents used; transference was necessary in all the experiments; both Madame Curie and Sir Edward Thorpe were troubled with insoluble deposits; and the accuracy of weighing was in the former case only 1 in 8000, and in the latter only 1 in 700. These disadvantages were absent from the method which we employed, viz. the conversion of radium chloride into radium bromide by heating it in a current of hydrogen bromide and vice versa; there was no transference and only gaseous reagents were used."

The material used by Ramsay and Gray was obtained from

Cornish pitchblende through the Radium Corporation, and consisted of 330 mgrms. of anhydrous radium barium bromide, containing about 70 per cent of radium bromide. These bromides were purified by the authors by treatment first with sulphuretted hydrogen whereby a small black precipitate, probably lead sulphide, was formed and removed. The solution was then acidified with sulphuric acid so as to precipitate the sulphates, which were dried and heated to redness in a mixture of carbon tetrachloride vapour and gaseous hydrogen chloride, whereby they were converted into chlorides. The chlorides were next converted into bromides by heating to redness for some hours in a current of hydrogen bromide.

The bromides thus obtained were submitted to fractional crystallisation whereby the barium was removed and the purified radium bromide was divided into a number of separate portions which were used for determining the equivalent. This was done as already indicated by determining the loss¹ of weight which ensued on converting a weighed quantity of bromide into chloride, and the gain¹ on converting the chloride into bromide. As the result of all this experiment, with the calculations following, the final result for the atomic weight of radium was 226.36, which is identical with the number found by Madame Curie.²

These then are some of the most striking facts which have become known to us about radium, and during the first year or two after the isolation of this curious substance no explanation was forthcoming which seemed to satisfy both chemists and physicists, for the simple reason that nothing of the kind had previously been dreamt of in their philosophy.

The results of Madame Curie's work showed that the phenomena exhibited by radium salts were due not to the molecule as a whole, but to the atom of the new element independently of the other elements with which it was associated. Thus equivalent quantities of chloride, bromide, and sulphate of radium show equal activity electrically.

It was immediately found that the radiations of radium are very complex, and unlike the cathode rays, some are not affected

¹ The quantities to be weighed being very small, usually 2 to 3 mgrm., a special balance was used, one form of which was described, p. 59, Part I.

² The value accepted at the present time is 225.97, but there is reason to believe that this may be low.

by a magnetic or electric field and they differ in the extent to which they may be stopped by metallic or other screens interposed in their path.

According to Professor Rutherford radio-active substances afford three types of radiation which he distinguished by the Greek letters, alpha α , beta β , and gamma γ .

The α -rays are readily stopped by tinfoil or a sheet of writing-paper, and travel only a short distance even through air, but are little influenced in direction by a magnet.

The β -rays are similar in character to the cathode rays produced in a vacuum tube (see p. 101).

The γ -rays resemble Röntgen or X-rays; they appear always to be associated with the β -rays.

At this point it will be well to explain briefly the principles of the methods which are employed in studying these radio-active substances. Three general methods have been used, and reference to them has already been made in the preceding account of the discovery of radium. The first depends on the action of the radiation on a photographic plate. The second on the luminosity produced when the rays strike the surface of certain substances, such as zinc sulphide (blende) or certain platinocyanides. The third process is the most important, as it lends itself to the purposes of exact measurement more readily than the other two. This is electrical and rests on the property possessed by the radiations of ionizing the gas or gases through which they pass. Ionisation means the production of positively and negatively electrified particles, which act as carriers of electricity.

An electroscope, much used by Professor Rutherford in his early work, is shown in the accompanying figure. Within a brass case, provided with a window W, is suspended a brass plate B connected by a rod D with the gold leaf C. It is supported

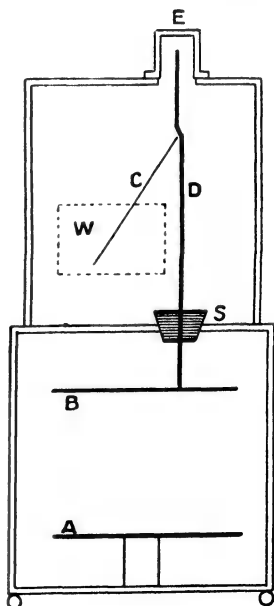


Fig. 47.

RUTHERFORD'S ELECTROSCOPE

by the plug of sulphur S, which is a very perfect insulator. One side of the lower box opens on a hinge, and access is thus gained to the lower plate A, which is connected through the case to earth. The gold leaf is charged to a suitable potential to give it a deflection of about 40° , and the cap E is then placed over the end of the rod. The active matter to be tested is placed on the plate A, and the rate at which the gold leaf falls is observed by means of a telescope having a scale of divisions in the eyepiece. The time taken for the leaf to pass between two points on the scale is noted by a stop-watch, and the average rate of movement per minute can be determined. The average rate of movement per minute is directly proportional to the ionisation current between the two plates A and B, that is to the intensity of the radiation emitted by the active substance on the lower plate. There is a small natural leak due to atmospheric ions, for which allowance is always made.

As to the α -rays some doubt was for a long time experienced as to their nature. But physicists were agreed that they consisted of particles of matter charged with electricity and projected with great velocity. The discovery of helium in association with the minerals showing radio-activity and from which radium was extracted, led Professors Rutherford and Soddy to suggest in 1902 that helium might be a product of the disintegration of the radio-elements. Soon after this Sir William Ramsay and Professor Soddy¹ discovered that helium is contained in the gases, oxygen and hydrogen, which are set free on dissolving radium bromide in water. And later it was proved, from evidence of its spectrum, that helium was definitely formed in a sealed tube containing radio-active material.

¹ Frederick Soddy was born at Eastbourne on September 2nd, 1877; he was educated at the University College, Aberystwyth, and Merton College, Oxford. He worked under Rutherford at McGill University, Montreal, from 1901 to 1903, and under Ramsay, at University College, London, from 1903 to 1904. Until 1914 Soddy was Lecturer in Physical Chemistry and Radio-activity at the University of Glasgow, and from 1914 to 1919 he occupied the Professorship of Chemistry at Aberdeen; in 1919 he was appointed Lees Professor of Inorganic and Physical Chemistry at Oxford. Soddy's chief contributions to chemistry are the development, in conjunction with Rutherford, of the idea of radio-active disintegration, and the clear enunciation of the Group Displacement Law which led to the concept of isotopes. In connection with the latter, Soddy not only invented the term "isotope," but also contributed the fundamental experimental verification of their existence. During recent years he has become interested in economic matters and has published a number of works on the subject of money. Soddy was elected to the Royal Society in 1910 and awarded the Nobel Prize for Chemistry in 1921.

The α -rays, therefore, consist of atoms of helium positively charged and ejected from the atom of radium with a velocity about $\frac{1}{18}$ the velocity of light; from experiments on the deflection of the α -particles in electrical and magnetic fields it has been shown that they each carry two unit positive charges.

The β -rays were discovered in consequence of the fact that they are drawn aside by a magnetic field. If an active preparation is placed in a short narrow lead tube it will cause a fluorescent patch to become visible on a screen coated with a platino-cyanide held above it. If the poles of an electro-magnet placed on either side are excited the phosphorescent patch is broadened out on one side showing that the rays causing the fluorescence have been deflected.

By reversing the magnetic field the broadening of the fluorescent patch takes place in the opposite direction. The deflection can also be shown by taking advantage of the photographic properties of these rays.

The β -rays consist of particles (electrons, see p. 103) carrying a negative charge. This can be observed by means of an ingenious device arranged by Strutt¹ and called the "radium clock." It consists of a glass tube evacuated as completely as possible by means of a mercury pump, and partially lined with tinfoil connected with earth.

In the vertical axis of this vessel is suspended, by a quartz rod, a small tube containing a radium salt in metallic connection with a pair of gold leaves attached to the lower end by means of a brass cap. The lower part of the tube containing the radium is smeared with phosphoric acid to render it con-

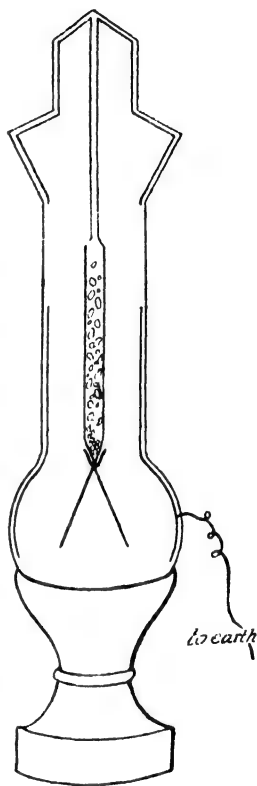


FIG. 48.
STRUTT'S RADIUM CLOCK

¹ The Hon. R. J. Strutt, now Lord Rayleigh, lately Professor of Physics in the Imperial College of Science, London.

ducting. While the negative β -rays are discharged into the glass of the tube, the gold leaves gradually acquire a positive charge, which they retain, if the vacuum is good, till they diverge sufficiently to touch the tinfoil lining of the bulb, when they instantly collapse. They then gradually get recharged, and the operation is repeated at intervals, the frequency of which depends on the amount and activity of the substance connected with the gold leaves. (*Philosophical Magazine*, 1903, p. 588.)

The radiations of thorium and radium designated α , β , and γ , are accompanied by an active substance which was found to be carried off in a current of air, and which, though it would pass slowly through paper, could be prevented from escaping by a thin sheet of mica. This seemed to agree with the properties of a gas, and it was proved by special experiments that the observed activity was not due to particles of dust. Further investigation showed that the "emanation," as it is called, possesses the properties of a chemically inert gas. This substance was named "niton" by Sir William Ramsay, who, notwithstanding its instability, placed it among the argon group of elements in the periodic scheme. The gas originating from radium is now called "radon."

According to Rutherford's disintegration theory of radioactive change a definite number of atoms of radium break up per second, each atom evolving an α -particle which ultimately becomes a helium atom, leaving behind the residue of the atom which forms the gas known as the "emanation" or radon. It seems to be agreed that the radium atom on disintegration to radon splits up into two parts only, one of which is the α -particle. The atomic weight of the resulting radon must be therefore the atomic weight of radium *minus* the atomic weight of helium or $226.0 - 4 = 222.0$

This question, however, as Sir William Ramsay remarked, can only be settled by appeal to experiment, and in 1910, in association with Dr. Whytlaw-Gray, and with the aid of a balance constructed on the same principle as the balance used for the estimation of the atomic weight of radium he proceeded to determine the density of radon.¹ To appreciate the extreme delicacy and difficulty of the operations involved it is necessary to read

¹ "The Density of Niton (Radium Emanation) and the Disintegration Theory," *Proc. Royal Soc.*, vol. 84 (1911), p. 536.

the original memoir in its entirety. It will be sufficient to state in this place a few facts connected with the enquiry.

To determine the density of a gas, four separate measurements are essential,—the volume, the temperature, the pressure, and the weight of the gas. The volume of radon which accumulates in a given time from a known weight of radium is a constant quantity and has been repeatedly measured. In the present case the total volume of radon obtainable for weighing scarcely exceeded 0.1 cubic mm. The weight of this volume on the assumption that the atomic weight is 222 is less than $\frac{1}{1400}$ mgrm. It is therefore evident that in order to weigh this minute quantity of gas with sufficient exactness a balance turning with a load not greater than $\frac{1}{100,000}$ mgrm. is a necessity. This seems an almost inconceivably small weight to attempt to measure when one considers that the limit of sensibility of a delicate assay balance is about $\frac{1}{200}$ mgrm.

The atomic weight of radon deduced from five series of experiments was as follows :

I.	II.	III.	IV.	V.	MEAN.
227	226	225	220	218	223

This is in excellent agreement with expectation, based on the known atomic weight and the supposition that radium disintegrates into radon and an α -particle only.

The same authors have shown that radon is liquefiable by cold, and its boiling-point under atmospheric pressure is -62° or 211° absolute. The critical temperature, that is the temperature above which the gas cannot be liquefied by pressure, is 104.5° or 377.5° absolute.

The liquid emanation is colourless, it causes the glass of the containing tube to phosphoresce brightly. On further cooling it sets to a solid which melts at -71° .

The emanation or radon, as it is generally called, though so definite a substance is even less permanent than radium itself, for while the life of radium extends to thousands of years, the period of half decay being calculated as 2000 years, the half-period of transformation of niton is only 3.85 days. Its immediate products of disintegration are α -rays which escape and a solid active deposit which is still more evanescent, having a half-transformation period of only 3 minutes. This substance, which has been labelled RaA, is transformed again in six stages till a product

is obtained which has been identified with the *polonium* separated from uranium residues by Madame Curie in her original investigation. There is good reason to believe that the final product of the disintegration of polonium is lead.

As already mentioned the proportion of radium found in a mineral bears a constant ratio to the amount of uranium present, and this seems to suggest that radium is formed by the disintegration of uranium. If this is the case it is obvious that if a specimen of a uranium compound were prepared free from radium it should be possible in course of time to recognise the production of radium in such a material. Experiments of this kind have been made, but the results showed that the change was too slow to admit the supposition of an immediate connection between radium and uranium. An intermediate substance has been detected, and it has been called *ionium*, but it has, according to Professor Soddy, an average life of about 30,000 years. It is not possible as yet to establish a direct relation between radium and pure uranium, but it appears that ionium is the parent of radium. While therefore much has been accomplished the history of radium is by no means yet complete. The story is further complicated by the fact that radium is not the only radio-active substance obtainable from uranium minerals. A substance called *actinium* was early recognised as being present, and this is also radio-active giving rise to an independent series of products.

The remarkable phenomena of radio-activity presented a problem of great complexity: elements had hitherto been regarded as the simplest forms of matter and yet here was a definite element like radium breaking up spontaneously into two other elements, helium and radon. The explanation of the observations was put forward in the daring Disintegration Theory proposed by Rutherford and Soddy in 1903. "On this theory, the atoms of the radio-elements, unlike the atoms of the ordinary elements, are not stable but undergo spontaneous disintegration accompanied by the expulsion of an α - or β -particle. After the disintegration, the resulting atom has physical and chemical properties entirely different from the parent atom. It may in turn be unstable and pass through a succession of transformations each of which is characterised by the emission of an α - or β -particle." This process goes on until eventually a stable non-radio-active element is reached. It must be remembered that

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when an α -particle is lost the atomic weight decreases by 4, but since the β -particle is an electron, having a very small mass, its loss results in no appreciable change in atomic weight.

As a result of much careful and difficult experimental work, over nearly forty years, it has been possible to determine the stages in the disintegration of the uranium series, which are represented in the following table. It should be mentioned that at one or two points branched disintegration takes place, that is it occurs in two different ways, but the main series only is given here.

Name.	Atomic weight.	Time of half-change.	Rays emitted.
Uranium I . . .	238.1	4.5×10^9 years	α
Uranium X_1 . . .	234	24.5 days	β
Uranium X_2 . . .	234	1.14 min.	β
Uranium II . . .	234	10^6 years (?)	α
Uranium Y . . .	230	24.6 hours	β
Ionium	230	7.6×10^4 years	α
Radium	226.0	1600 years	α
Radon	222	3.82 days	α
Radium A	218	3.05 min.	α
Radium B	214	26.8 min.	β
Radium C	214	19.7 min.	β
Radium C'	214	10^{-6} sec.	α
Radium D	210	25 years	β
Radium E	210	5.0 days	β
Radium F (Polonium) .	210	136.3 days	α
End product (Lead) . .	206	—	Inactive

It has been mentioned that the radio-active element actinium is always found in uranium minerals, and it is considered probable that it originates from uranium as a result of a branch disintegration of the element uranium X_1 . Actinium gives a series of products, of varying degrees of stability, one of them as in the case of radium being an inert gas. In the near future more will probably be known concerning the actinium series, since the element protoactinium, believed to be its immediate precursor, has recently been obtained in appreciable quantities in what is claimed to be a pure state.

Thorium and its compounds have long been known to be radio-active, and this element is the parent of an independent series of products resulting from radio-active disintegration accompanied by α , β and γ -rays. As already indicated one of these is an inert gas; it is called "thoron" and is identical chemically, although not in radio-active properties, with radon. The atomic weight of thorium is 232.1 and after the emission of six α -particles and four β -particles it yields an inactive end-product with an atomic weight of $232 - 6 \times 4 = 208$; this point will be considered later.

Incandescent gas-mantles are impregnated with a thorium compound (see chapter XVIII) and so they exhibit the phenomena of radio-activity; if a mantle is placed on a photographic plate in the dark and then developed, the effect of the radiations are evident in a reproduction of the mantle fabric on the negative.

The discovery of some forty radio-elements with atomic weights lying between 206 and 238 raised a serious problem in connection with the periodic classification, since there were not nearly enough spaces to accommodate them all as separate elements. When their chemical properties became known, however, and chiefly as a result of the work of Alexander Fleck, carried out in the University of Glasgow under the direction of Professor Soddy, it became clear that "not a single one of the radio-elements . . . has a peculiar chemical nature unshared by others. All are chemically indistinguishable from one or other of the elements occupying the last twelve places of the periodic table from thallium to uranium." For example, radium B, radium D, actinium B, and thorium B all have identical chemical properties, which incidentally are the same as those of the common element lead; these five elements, therefore, may be regarded as occupying the same position in the periodic table in spite of their atomic weights lying between 207 and 214. Similarly, the three radio-active emanations already mentioned, belonging to the radium, actinium, and thorium series, are all inert gases, having different atomic weights—222, 219, and 220, respectively—but occupying the same place in the Zero Group of the periodic table.

When the known radio-active elements were arranged in the periodic classification according to their chemical properties, and not by their atomic weights, a striking generalisation known as

the Group Displacement Law becomes evident ; its clear enunciation is mainly due to Soddy (*Chemical News*, February 28th, 1913), although Dr. A. S. Russell, Professor K. Fajans, and Professor G. von Hevesy contributed important ideas towards its development. According to this law, when a radio-element emits an α -particle, which carries two positive charges, it moves two places to the left in the periodic table, that is to say its atomic number decreases by two ; the loss of a β -particle, with its one negative charge, however, results in a shift of one place to the right, corresponding to an increase of unity in its atomic number. It is evident, therefore, that the emission of one α and two β -particles in succession brings an element back to its original place in the table, although its atomic weight is now decreased by four units. To elements having the same atomic number and thus occupying the same position in the periodic table Soddy gave the name "isotopes" (Greek, equal place). It was supposed that "they are chemically identical, and save only as regards the relatively few physical properties which depend on atomic mass directly, physically identical also." Their radio-active properties are, however, quite different.

One of the remarkable consequences of the Group Displacement Law was that the end products of both the uranium and thorium series of radio-elements were seen to occupy the same position in the periodic table as the element lead, and so they should be isotopes and identical with it chemically. An examination of the atomic weights showed, however, that whereas that of uranium-lead should be 208, that of thorium-lead should be 206, compared with 207.2 for common lead. Now, it is known that both uranium and thorium minerals are always associated with a certain amount of lead, no doubt the result of radio-active disintegration proceeding over many millions of years ; if the brilliant speculations of Soddy were correct, therefore, the lead associated with these two minerals should have atomic weights different from one another and from that of ordinary lead obtained from non-radio-active sources. The accurate determination of atomic weights requires great skill and experience, but in spite of this Soddy, in conjunction with Mr. H. Hyman of the University of Glasgow, undertook an examination of the lead obtained from the thorium-rich mineral found in Ceylon, and known as "thorite" ; they found that its atomic weight was definitely greater than that of ordinary lead. A sample

of the lead was also sent to Professor Hönigschmid of Vienna, who was an expert in atomic weight determinations, and he found it to have an atomic weight of 207.77. At the same time Fajans had sent one of his pupils, Mr. Lambert, to the United States in order to study the same atomic weight of uranium lead under the late Professor T. W. Richards, then the world's leading authority on the subject; the results published in 1914 showed that the atomic weight of lead from pitchblende and from uraninite was about 206.5. Further experiments have all tended to confirm the difference in the atomic weights of lead originating from uranium and thorium, and the results are exactly as expected from the Group Displacement Law. The following summary of the most reliable measurements is of interest.

ATOMIC WEIGHT OF LEAD FROM URANIUM MINERALS

Origin.	Atomic weight.	Investigator.
Pitchblende, Joachimsthal	206.57	Richards and Lambert, 1914.
Uraninite, N. Carolina	206.40	„ „ „
Uraninite, Morogoro	206.05	Hönigschmid and Horovitz, 1915.
Pitchblende, Katanga	206.05	Hönigschmid and Birkenbach, 1923.
Cleveite, Norway	206.08	Richards and Wadsworth, 1916.
Bröggerite, Norway	206.12	Richards and Wadsworth, 1916.
Kolm, Sweden	206.01	Baxter and Bliss, 1930.

ATOMIC WEIGHT OF LEAD FROM THORIUM MINERALS

Therite, Ceylon	207.7	Soddy, 1915.
Thorite, Ceylon	207.77	Hönigschmid, 1917.
Thorite, Norway	207.9	Hönigschmid, 1919.

Specimens of lead from minerals containing both uranium and thorium were found to have atomic weights between the two extreme values; thus Richards obtained 206.34 for lead from a mixed Australian mineral. Ordinary lead having an atomic weight of 207.2 is now known to be a mixture of several isotopes, of which those with atomic weights of 206 and 208 predominate.

This definite proof of the existence of non-radio-active isotopes

of the element lead has resulted in the search for and the discovery of many other elements, not related in any way to the radio-elements, which are actually mixtures of isotopes. The development of the concept of isotopes in connection with non-radio-active elements can well be described in the words of Dr. F. W. Aston, who has himself been responsible for a great deal of the work, in a lecture before the Chemical Society on April 7th, 1921 (*Journal*, 1921, p. 677). "The theory of isotopes was triumphantly vindicated during the war by the researches of Soddy, Richards, and Hönigschmid, and others on the atomic weights of lead found in various radio-active minerals. Quantities were obtained ample for the most accurate determinations by chemical methods, and the atomic weights were found to differ from each other and from that of ordinary lead by quantities altogether outside possible experimental error.

"Long before this convincing proof was forthcoming the theory of isotopes was discussed with the greatest interest in connection with atomic weights in general. If isotopes occurred among the heavy elements, why should they not be possible among the lighter non-radio-active ones? In which case elements with fractional atomic weights might clearly be mixtures, the constituents having atomic weights equal to whole numbers. This explanation was an attractive one for the curious jumble of whole numbers and fractions in atomic weights, when referred to oxygen as 16, has always been a serious stumbling-block in the way of any simple theory of atom-building. The accurately determined atomic weight of chlorine, 35.46, has certainly nothing to recommend it. It is reminiscent of the number of square yards in a square rod, pole, or perch, but the idea of Nature working on the same lines as the British weights and measures is an eminently unattractive one.

"The first support of the isotope theory among non-radio-active elements was given by the anomalous behaviour of the inactive gas neon when analysed by Sir J. J. Thomson's method of positive rays (1913, see p. 105). This peculiarity was that, whereas all elements previously examined give single, or apparently single, parabolas, that given by neon was definitely double. The brighter curve corresponding roughly with an atomic weight of 20, the fainter companion with one of 22, the atomic weight of neon being 20.20. In consequence of the reasoning adduced from the characteristics of the line 22, the discoverer was of the

opinion that it could not be attributed to any compound, and that therefore it represented a hitherto unknown elementary constituent of neon. This agreed very well with the idea of isotopes which had just been promulgated, so that it was of great importance to investigate the point as fully as possible.

"The first line of attack was an attempt at separation by repeated fractionation over charcoal cooled with liquid air, but even after many thousands of operations the result was entirely negative. It is some satisfaction to know that this result was inevitable, as Professor Lindemann has recently shown on thermodynamical grounds. Fractional diffusion through pipe-clay was more effective and gave a positive result. An apparent difference of density of 0.7 per cent between the lightest and heaviest fractions was obtained after an exceedingly laborious set of operations. When the war interrupted the research, it might be said that several independent lines of reasoning pointed to the idea that neon was a mixture of isotopes, but none of them could be said to carry the conviction necessary in such an important development.

"When the work was recommenced, attention was again directed towards positive rays, for it was clear that if any analysis could be made with such accuracy that it could be demonstrated with certainty that neither of the two atomic weights so determined agreed with the accepted chemical figure, the matter could be regarded as settled. This could not be done with the parabolas already obtained, but the accuracy of measurement was raised to the required degree" . . . by improvements in the technique. "Positive rays are sorted out into a thin ribbon by means of two parallel slits . . . and are then spread into an electric spectrum by means of charged plates. . . . A portion of this spectrum deflected through an angle . . . is selected by a diaphragm and passed between the circular poles of a powerful electro-magnet, the field of which is such as to bend the rays back again. The result of this is that rays having a constant mass . . . will converge to a focus, and that if a photographic plate is placed "in a suitable position" *a spectrum dependent on mass alone* will be obtained. On account of its analogy to optical apparatus, the apparatus has been called a positive ray spectrograph and the spectrum produced a mass-spectrum."

By means of the mass spectrograph Aston was able to study

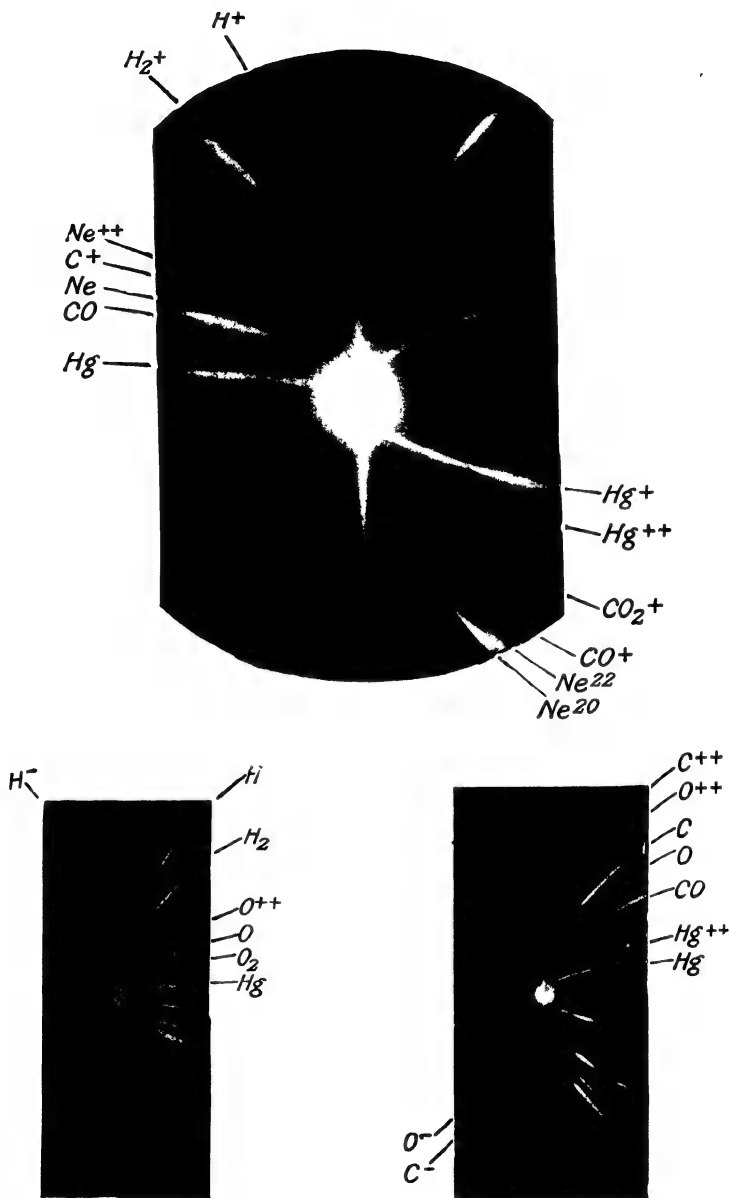


FIG 49 — POSITIVE-RAY PARABOLAS

(From Aston's "Mass Spectra and Isotopes", by courtesy of Messrs. Edward Arnold & Co.)

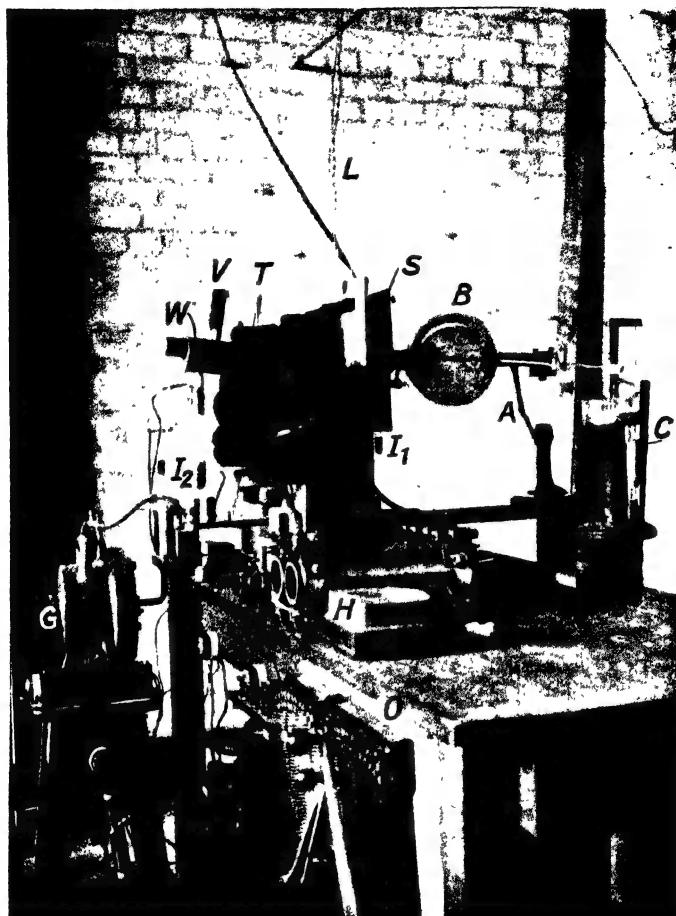


FIG. 50 —ASTON'S FIRST MASS SPECTROGRAPH, NOW IN THE SCIEN
KENSINGTON, LONDON

(B is the discharge tube, I_1 and I_2 are charcoal tubes, and G a pump for maintaining a vacuum, M is an electro-magnet, and W the camera for photographing the mass-spectra)

the isotopic constitution of a large number of elements, for when an element consists of a mixture of isotopes having different masses, each isotope will register its presence on the photographic plate according to its mass only, quite apart from its chemical identity. Over eighty elements have been tested for isotopes, either by this means or by a method depending on the study of ordinary spectra which has proved more satisfactory in certain cases, but only twenty-two of those examined have been found to consist of one type of atom only; all the others are mixtures of two or more, in one instance as many as eleven, isotopes. Even oxygen, which was for a long time regarded as consisting of a single type of element and so was used as the standard for the determination of atomic weights, has now been found to be made up of three isotopes of masses very close to 16, 17, and 18 in the proportions of approximately 3000 to 1 to 6, respectively.

It may be noted here, although the matter will be considered again later, that the atomic weights of individual isotopes have been found, by means of the mass spectrograph, to be invariably very close to whole numbers; the variety of fractional values in the atomic weights quoted on p. 109 is generally to be attributed to the fact that in nature elements exist as mixtures of isotopes in various proportions.

One of the most important discoveries in the field of isotopes has been in connection with the simplest element of all, hydrogen; it has been shown recently to consist of at least two isotopes of atomic weights approximately 1 and 2. The knowledge concerning the heavier isotope, sometimes called "heavy hydrogen," apart from its intrinsic interest, is having a profound influence on modern chemistry, so much so that it has been stated¹ "some chemists consider its discovery to be possibly the greatest advance in chemistry made in the century." Since it is difficult so soon to assess the relative values of great discoveries, this statement may be a slight exaggeration, nevertheless the subject is so important and interesting that it merits further consideration here.

When Aston determined the atomic weight of hydrogen by the mass spectrograph he obtained a value of 1.00777, which was in excellent agreement with the chemical value 1.00778, based on the supposition that oxygen was a uniform element of

¹ Professor M. Polanyi, Royal Institution Discourse, November 23rd, 1934 . . . printed in *Nature*, January 5th, 1935.

atomic weight 16.0000 ; the discovery of the isotopes of oxygen, however, showed that the average chemical atomic weight of ordinary oxygen, being a mixture of three isotopes of masses 16, 17, and 18, should be 16.0035, and so the chemical atomic weight of hydrogen was 1.00799. The discrepancy between this value and that obtained by the mass spectrograph could not have been due to experimental error, and hence it was suggested by Professor R. T. Birge and Dr. D. H. Menzel, in the United States of America, that ordinary hydrogen might contain an isotope of mass 2, which if present to the extent of about one part in five thousand would account for the difference in the two atomic weights. In December, 1931, Professor H. C. Urey, in conjunction with Dr. G. M. Murphy and Dr. F. G. Brickwedde, in New York, announced the detection of two very faint lines in the ordinary spectrum of hydrogen, the latter being the residue from the evaporation of liquid hydrogen, which corresponded to the presence of the heavy isotope of mass 2.

This result would not have been so important were it not for the further discovery made shortly afterwards by Professor Urey that when an electric current is passed through water, the hydrogen gas given off by electrolysis, at the cathode, contains relatively more of the light isotope, so that in the residual liquid there gradually accumulates a larger proportion of the heavier isotope. An examination of waters obtained from commercial electrolytic cells, which had been in use for some years, showed that in fact they did contain more of the heavier form of hydrogen than did ordinary water. Following on the work of Professor G. N. Lewis of California, Professor H. S. Taylor, at Princeton, United States, and his collaborators electrolysed about $2\frac{1}{2}$ tons (500 gallons) of commercial electrolyte containing 0.03 per cent of the heavier isotope until only 3 ounces were left—a stupendous task—and they found that in this residue 99 per cent of the hydrogen was in the form of the heavy isotope and only 1 per cent as the lighter form.

The importance of this achievement was that there became available appreciable amounts of the heavy isotope of hydrogen, so that its properties could be compared with that of ordinary hydrogen and some remarkable differences have been observed. In order to distinguish between the two isotopes the heavier one, of mass 2, is called *deuterium* (Greek, the second) and is given the symbol D ; the oxide, D_2O , is the heavy hydrogen analogue

of ordinary water, which is almost exclusively H_2O , and is frequently called "heavy water." This is the product obtained by Lewis and by Taylor by electrolysing away ordinary water, until the heavy form was left in a practically pure state; this substance is now available commercially, and is being much used for experimental work. The physical properties of heavy water are somewhat different from those of ordinary water; the former has a density of about 10 per cent greater than the latter, in agreement with the difference in the molecular weights, viz. $\text{D}_2\text{O}=(2\times 2)+16=20$, and $\text{H}_2\text{O}=(2\times 1)+16=18$. The boiling and freezing points of heavy water are 101.4° and 3.82° C., compared with 100.0° and 0.0° C., respectively, for water consisting of the light isotope.

These physical differences, although striking, were not unexpected, but the surprising discovery came in connection with the chemical properties. Until the discovery of deuterium it had always been considered that isotopes of an element, having the same atomic number and occupying the same position in the periodic table, were identical chemically, but it now became evident that this was not rigidly true. Although deuterium undergoes the same reactions as the lighter form of hydrogen with which chemists have long been familiar, the molecules invariably react more slowly, and this is generally true of its compounds. It was at first thought that this difference was due to the difference in the speeds of the molecules, since it can be shown that the heavier molecule must move more slowly, and so meets other molecules with which it can react less frequently, than the light one. Since the ratio of the masses of the hydrogen isotopes, 2 to 1, is much greater than that of any other pair of isotopes, the difference in chemical reactivity might be expected to be greater than in other cases. A further examination of the results showed, however, that this explanation was not adequate, and another had to be sought for; it has been found in the important "Principle of Uncertainty," now playing an important part in physical and philosophical discussions.

A clear exposition of the arguments has been given by Professor M. Polanyi, of Manchester University, in his Royal Institution Discourse already mentioned (footnote, p. 151), from which the following is a quotation: "The uncertainty principle states that no information can be obtained about the velocity of a particle the position of which is known with absolute

certainty. Certain information about the velocity can be arrived at, if we admit a certain *inaccuracy* of position. Thus the two uncertainties remain tragically linked together in the formula

Inaccuracy of position \times inaccuracy of velocity = constant.

Our information on position and velocity has in it a compound inaccuracy which is irreducible.

"From this uncertainty, however, we can derive a dynamical principle latent in all matter, which acts against a force holding a particle, and in so doing modifies the effects of the force. It will also appear that the effect of this dynamical principle depends on the mass of the particle, and is therefore different for two atoms giving rise to identical forces, but differing in mass. We shall then see that this is the true reason why the two [isotopic] hydrogen atoms are so different.

"A fictitious experiment will enable us to realise the dynamical principle in question. Suppose we attempt to defeat the uncertainty principle by sheer force. We take an atom and hold it at rest in some fixed position. If we succeed in doing this, we would obviously overthrow the law of uncertainty. The position of our atom would be exactly known and, since we suppose it to be held at rest, its velocity would also be known to be exactly zero. The law of uncertainty predicts that our experiment will fail. Any force trying to keep an atom in a fixed position would be defeated by a power given to the particle to defend its uncertainty. It will defend it by starting to vibrate. The tighter we try to hold the atom to stop this vibration the more violent would the vibration become. No force would be strong enough to keep the particle in place motionless.

"The uncertainty law thus leads to the following postulate : Any particle restricted to a definite range of positions is necessarily in motion ; the range of velocities contained in this motion will be the wider the narrower the restriction of positions ; that is

Range of positions \times range of velocities = constant.

In nature atoms are restricted in position when linked up to chemical compounds. Such restriction, we must conclude, will give rise to an uncertainty motion of the atoms. All molecules will hence contain a certain amount of uncertainty motion, and also, since the motion has kinetic energy attached to it, a certain

amount of corresponding energy. We might also postulate that the more restricted the positions of the atoms in the molecule are, that is, the stronger the bonds that hold the atoms in position, the more violent will be the uncertainty motion, and hence the greater will be the [permanent] energy content of the molecule due to uncertainty.

“Next to bond strength, atomic mass will influence the uncertainty motion. This influence of mass is contained in the constant of the uncertainty formula, which can be written :

$$\text{Range of positions} \times \text{range of velocities} = \frac{\text{universal constant}}{\text{mass}}.$$

Thus the composite uncertainty on the left-hand side of the equation is smaller the larger the mass of the particle. Hydrogen of mass 1 will have a compound uncertainty twice as large as hydrogen of mass 2. Under equal conditions, therefore, the uncertainty motion and [permanent] energy of this motion will be larger for light hydrogen than for heavy hydrogen ; in corresponding molecules containing the two sorts of hydrogen, there will be more [permanent] ‘uncertainty energy’ present when the molecule contains ordinary hydrogen than when it contains the heavy isotope.

“Compare, for example, ordinary water with heavy water. For ordinary water the ‘uncertainty energy’ amounts to 13,097 calories ; for heavy water it is only 9,527 calories. Since the uncertainty energy is only present in molecules, and vanishes when the atoms are set free [since their position is not restricted], it follows that less work is needed to break up an ordinary water molecule into free atoms than to separate the atoms of heavy water. . . . From such differences in the [permanent] energy contents of the corresponding molecules, all the differences in the chemical properties of the two hydrogens arise. . . .

“A molecule undergoes chemical reaction only if it happens to accumulate a certain critical amount of energy. The molecule has to wait until, in the course of the constant fluctuation of energy caused by heat motion, it happens to get an especially big share of energy equal to this critical energy. As soon as it has swallowed this, it goes to pieces—that is chemical reaction.

“Now suppose we have two molecules, one a compound of ordinary hydrogen, and the other the corresponding compound of heavy hydrogen. Let both molecules wait side by side until,

by a fortunate fluctuation of thermal motion, they acquire the critical energy necessary for reaction. The ordinary hydrogen molecule is obviously in a better position in this competition, since it has a start on account of its greater permanent energy. The energy required by it is correspondingly smaller, and it will have an earlier chance to get this smaller quantity. It will, therefore, react before its competitor, the heavy hydrogen compound. This is the reason for the lower reactivity of heavy water, and of other heavy hydrogen compounds."

Not only is deuterium important because it permits of a correlation of its properties with modern fundamental theories of physics, but also because it is proving a valuable weapon in the attack on many scientific problems. The use of heavy hydrogen is equivalent to putting an indelible mark on some of the hydrogen atoms which is always capable of detection, and so it is possible to trace the history of these atoms in chemical and biological processes. In this way important information concerning the mechanism of many chemical reactions has already been obtained and much progress is likely to be made in the near future. It is, unfortunately, not possible to deal with the subject more fully here, but it is hoped sufficient has been said to indicate the importance of the discovery of the heavy isotope of hydrogen.

CHAPTER VIII

THE STRUCTURE AND DISINTEGRATION OF ATOMS

IN their passage through matter α -particles, produced from radio-active materials, as a general rule follow a straight course, but very occasionally, say about once in ten-thousand, a particle is violently deflected out of its course. This simple, although quite definite, observation led Rutherford in 1911 to suggest that the whole mass of an atom was concentrated on an extremely minute *positively* charged nucleus, estimated to have a volume of only a thousand-million-millionth part of that of the atom as a whole. When an α -particle passes through matter it is affected only slightly unless it happens to come near the nucleus of an atom, when the powerful repulsion between it and the positively

charged α -particle results in the latter being turned completely out of its line of movement. Since the nucleus occupies such a small space it is easy to understand why only a small proportion of α -particles are deflected, the majority continuing their progress in straight lines.

As a result of the work of Moseley (p. 120) and of others it had been concluded in 1913 that the number of positive charges on the nucleus was equal to its atomic number, that is its ordinal number in the periodic table; from the extent which α -particles are deflected it is possible to calculate the magnitude of this charge, and experiments made by Dr. J. Chadwick, in Rutherford's laboratory in Cambridge, showed that it was in fact the same as the atomic number of the element causing the deflection.

Since an atom as a whole is electrically neutral there must be present negative particles, that is electrons, equal in number to the positive charge on the nucleus; it is supposed that these are arranged in some manner in what may be termed "orbits" or "shells" in the relatively large space around the minute nucleus. In view of their small mass these "orbital electrons" offer no obstacle, of course, to the path of α -particles. The nucleus theory of the atom, as developed by Rutherford, forms the basis of the modern views of atomic structure. It offers, incidentally, a simple explanation of the existence of isotopes; these have the same nuclear charge, although the masses of the nuclei may be different, and it is the nuclear charge, equal to the ordinal number of the element in the periodic table, which in general determines the chemical properties of an element. Further reference to this matter will be made later.

The view that the atom is made up of positive and negative charges brings us to a consideration of the possibility of transforming one atom into another: this had been the dream of alchemists for hundreds of years, but¹ "since the development of the atomic theory on an experimental foundation by Dalton, the progress of chemistry has been based on the central idea of the permanency and indivisibility of the atoms of the elements. The whole experience of chemistry for nearly a century has shown clearly that it was impossible to break up the atoms of the elements by the application of ordinary chemical and physical processes. . . .

¹ Quoted from Rutherford's lecture to the Chemical Society, *Journal*, 1922, p. 400.

"The discovery of the instability of the radio-active elements was the first severe shock to the idea of the permanency of all atoms. This radiating property is, however, confined mainly to the two heaviest elements, uranium and thorium, and their long series of descendants, and is only shown by two other elements, potassium and rubidium, and then only to a minor extent. Apart from these exceptions, the great majority of the atoms appear to be highly stable structures, and to remain unaltered under ordinary conditions in this earth for periods of probably thousands of millions of years. . . .

"Radio-activity has . . . at the same time given us in the swift α -particles . . . a powerful method of probing the inner structure of the atom. . . . The swift α -particle from radium and thorium, which is by far the most concentrated source of energy known to us, seems the most likely agent to succeed in an attack on the strongly bound " nuclei of atoms, in the hopes of bringing about disintegration.

"The α -particle is expelled from radium with a velocity of about ten thousand miles per second, and thus has a speed twenty thousand times greater than that of a swift rifle bullet. Mass for mass, its energy of motion is four hundred million times greater than that of the bullet.

"Whilst no doubt an α -particle fired directly at a heavy nucleus may penetrate its structure, its energy may at that stage be too small to cause disruption. The attack on the lighter atoms is much more promising, for the repulsive forces are so much smaller that the α -particle may still retain much of its energy on entering the nuclear structure. . . .

"The first observation which has to do with the main subject of my lecture was made some years ago. When the α -rays from a strong radio-active source pass through dry gases like oxygen or carbon dioxide, a small number of weak scintillations are observed on a [zinc sulphide] screen beyond the range of the α -particles. These 'natural' scintillations are believed to be due to atoms of hydrogen coming from the source, and probably result from a slight hydrogen contamination. . . . If, however, dry air is substituted for oxygen or carbon dioxide, the number of scintillations is increased three or four times. This additional effect was found to be due to the presence of nitrogen, and was shown in a correspondingly greater degree by chemically prepared nitrogen. By suitable arrangements, it was found that

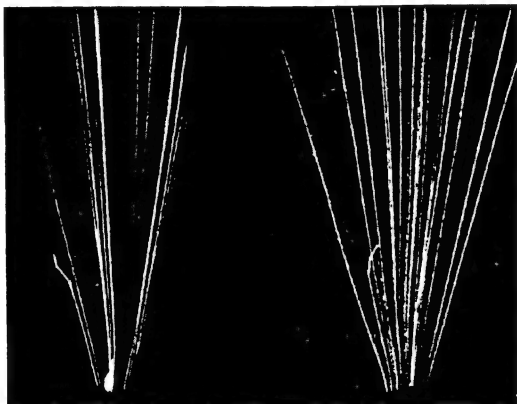


FIG. 51 — PASSAGE OF α -PARTICLES THROUGH NITROGEN
(Showing occasional disintegration of a nucleus of the
latter into a proton and a heavier particle)

(By courtesy of Professor P. M. S. Blackett, and the Royal Society)

the particles causing these scintillations were bent by a magnetic field to about the extent to be expected if they consisted of swift charged H-atoms. It seemed probable from the beginning that these additional H-atoms, which appeared only in dry nitrogen and not in oxygen or carbon dioxide, must have their origin in a disintegration of the nitrogen nucleus by collision with a swift α -particle."

An extension of the observations, just described in the words of Rutherford, in conjunction with Chadwick, carried out between 1922 and 1924, showed that all the elements between boron and potassium, inclusive, with the exception of carbon and oxygen, and possibly lithium and beryllium, could be disintegrated by the action of swift α -particles resulting in the emission of the long-range H-particles carrying a positive charge. These particles, which it will be seen later are important in connection with the problem of the structure of atomic nuclei, are called "protons"; they are actually hydrogen atoms of unit mass, which have lost their one orbital electron and so acquired a unit positive charge.

There is now no doubt that impact with α -particles results in the ejection of protons from the nuclei of certain atoms, and that a definite artificial disintegration of an atom was first brought about in this way. The extent of this disintegration is, however, minute, as it appears that for every million α -particles only about twenty collisions are effective. The nature of the process occurring has been made clear from photographs, taken independently by Dr. P. M. S. Blackett, in Cambridge, and by Professor H. S. Harkins in Chicago, in which the tracks of the α -particles before and after impact, in nitrogen, are made evident by the ionisation they produce. Most of the tracks (Fig. 51) are straight lines, showing that the α -particles have not suffered collision, but a few show definite branching; in these the α -particle track has disappeared and two others have formed. One of these is a long track, undoubtedly due to the long range, light proton, and the other, much shorter, is evidently caused by a much heavier nucleus. When a nitrogen nucleus is struck by an α -particle it evidently first engulfs the latter, and then the resulting unstable complex disintegrates immediately giving out a proton, thus :

	$\alpha\text{-particle} + \text{nitrogen nucleus} \longrightarrow \text{complex} \longrightarrow \text{proton} + \text{heavier nucleus.}$			
Mass	4	14	1	17
Charge	2	7	1	8

It will be noted that the total masses and electrical charges before and after impact must, of course, remain unchanged ; the mass of the " heavier nucleus " product of the disintegration is clearly 17, and its nuclear charge, and hence atomic number, is 8. It must, therefore, be an isotope of oxygen having an atomic weight of 17, which is known to be present to a small extent in ordinary oxygen gas (see p. 151). The amount of oxygen produced from nitrogen in this way is so minute as to make it quite impossible to verify its presence by ordinary methods, but the evidence of the tracks and certain calculations based on the masses and velocities of the various particles lead definitely to the conclusion that nitrogen has been transmuted into oxygen to a minute extent. Similar changes, involving an increase of three in the mass and of unity in the nuclear charge, probably take place with the other elements studied by Rutherford and Chadwick. These experiments are of great significance as showing definitely that the transmutation of one atom into another is possible ; they also suggest that the proton, with a mass of unity, is as might be expected, since so many atomic weights are almost whole numbers, a constituent of many atomic nuclei.

A number of observers found that when certain light elements, particularly beryllium and boron, were bombarded with α -particles, obtained from polonium, there was emitted what appeared to be radiations of great penetrating power ; these radiations were able to eject protons with considerable velocity from various atoms. For some time the nature of these radiations was a mystery, but in 1932 Dr. Chadwick put forward the suggestion that these so-called radiations consisted of particles of mass nearly equal to that of the proton, but having *no electrical charge* ; these particles were called " neutrons," their existence, as a unit of nuclear structure, having previously been frequently postulated. It is because these neutrons have no electrical charge and produce no appreciable ionisation, that their detection and identification has been found so difficult. Chadwick considers that the neutron arises from the disintegration of a complex nucleus of beryllium or boron following the capture of an α -particle, thus :

	α -particle + beryllium nucleus \longrightarrow complex \longrightarrow neutron + carbon nucleus.			
Mass	4	9	1	12
Charge	2	4	0	6

The product of this disintegration in which a neutron is emitted must be a nucleus of carbon, since it has a charge of 6 units ; as the mass is 12, it happens to be the same as the common form of the element carbon. A study of the masses and velocities of the particles before and after impact lends strong support to this view. The atom boron undergoes a similar transformation process leading to a neutron and ordinary nitrogen. The mass of the neutron has been found to be 1.0067, as compared with 1.0072 for the proton, and there is now little doubt that it must be regarded as a unit of atomic structure.

It has been already mentioned that the so-called penetrating radiations, which proved to consist of neutrons, were able to cause the ejection of a proton from certain atoms ; this process is evidently a disintegration resulting from impact without capture, so that the product is a nucleus having a mass of one unit less than that of the one struck, thus :

$$\text{Nitrogen nucleus} + \text{neutron} \longrightarrow \text{neutron} + \text{proton} + \text{carbon nucleus.}$$

Mass	14	1	1	1	13
Charge	7	0	0	1	6

In other cases, even with the same element, e.g. nitrogen, the neutron is captured, and the resulting complex disintegrates giving an α -particle, thus :

$$\text{Nitrogen nucleus} + \text{neutron} \longrightarrow \text{complex} \longrightarrow \alpha\text{-particle} + \text{boron nucleus}$$

Mass	14	1	4	11
Charge	7	0	2	5

Evidence has also been obtained of complete disintegration resulting from neutron bombardment: a carbon nucleus (mass 12), for example, in a non-capture collision with a neutron breaks up into three α -particles (each of mass 4).

Another remarkable example of atomic disintegration was discovered by Dr. J. D. Cockroft and Dr. E. T. S. Walton, working in the Cavendish Laboratory at Cambridge. These workers had developed an important technique for the production of protons of high velocity and when the latter were allowed to fall on to a layer of lithium oxide there was produced a stream of long-range particles which gave scintillations on a zinc sulphide

screen ; from their properties these were undoubtedly α -particles and the disintegration occurring appeared to be :

	Lithium nucleus + proton \longrightarrow complex \longrightarrow 2 α -particles.		
Mass	7	1	2×4
Charge	3	1	2×2

Boron and fluorine nuclei, amongst others, are also able to capture fast protons and disintegrate giving α -particles ; it is of interest to note that the largest emissions of α -particles were obtained from elements of atomic weight represented by the general expression $4n+3$, where n is a whole number ; lithium, boron, and fluorine, of atomic weights 7, 11, and 19 respectively, fall into this category. It seems probable that the nuclei consist of a whole number (n) of α -particles together with three protons ; the capture of another proton leads to the formation of a new α -particle by the four protons and this is immediately ejected.

The discovery of the heavy isotope of hydrogen (deuterium) and the possibility of obtaining *deuterons*, that is nuclei of deuterium having a mass of approximately two units and a unit positive charge, has led to further developments in disintegration. High velocity deuterons provide very effective missiles, since they are twice as heavy as protons, and by means of them a number of disintegrations and transformations have been achieved ; amongst the most interesting of these is the apparent formation of new isotopes of both hydrogen and helium, each having a mass of three, by the impact of rapidly moving deuterons on the deuterium nucleus itself, which is of course also a deuteron, thus :

	Deuteron (fast) + deuteron \longrightarrow new hydrogen nucleus + proton.			
Mass	2	2	3	1
Charge	1	1	1	1

and	Deuteron (fast) + deuteron \longrightarrow new helium nucleus + neutron.			
Mass	2	2	3	1
Charge	1	1	2	0

The world of science was still recovering from the startling shocks of the discovery of the heavy hydrogen isotope, the neutron and the positron (see p. 107), and of the disintegrations and transformations brought about by protons, neutrons, and deuterons, when another spectacular and scientifically important phenomenon was observed. In the course of experiments early

in 1934 on the action of α -particles from polonium on thin layers of various elements, Mme Irène Curie-Joliot, the daughter of Mme Curie the discoverer of radium, and her husband M. Joliot, working in Paris, noted that during the course of the bombardment of boron, magnesium, and aluminium both neutrons and positrons were emitted; this was not very surprising, but when the source of the α -particles was removed the emission of positrons continued for an appreciable time, gradually decreasing in intensity. The products of α -particle bombardment were thus behaving as "artificial" radio-elements, different only from the natural radio-elements in their giving off positrons (positive electrons), instead of α -particles or β -particles (negative electrons). This striking phenomenon has been called "artificial" or "induced" radio-activity. The active elements usually have a short life-period, generally less than twenty minutes, but none the less the decay of the activity occurs in the normal manner found with the radio-active elements of high atomic weight. It has been suggested that the bombardment process may be represent as:

Aluminium nucleus + α -particle \longrightarrow radio-phosphorus nucleus + neutron.				
Mass	27	4	30	1
Charge	13	2	15	0

followed by the gradual spontaneous disintegration of the artificially produced radio-phosphorus after removal of the source of the α -particles:

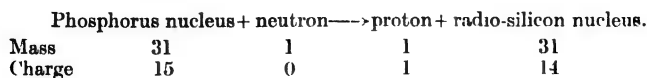
Radio-phosphorus nucleus \longrightarrow silicon nucleus + positron.			
Mass	30	30	0
Charge	15	14	1

It will be observed that the mass of the positron, which is very small, can be neglected, so that the final nucleus, silicon, has a mass of about thirty units. Since the artificial radio-element is believed to be an isotope of phosphorus it should have the same chemical properties as and be inseparable from the latter. Some proof of this was obtained by exposing aluminium foil to α -particles, and then dissolving rapidly in acid; sodium phosphate and a zirconium salt were added in order to precipitate zirconium phosphate, which was found to possess the new radio-activity. The radio-element produced from aluminium, therefore, appears to have the chemical properties of ordinary

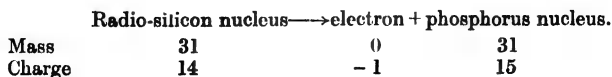
phosphorus, although having a differently constituted nucleus, of mass 30 as compared with 31, it is unstable and disintegrates spontaneously. Similar evidence has been obtained that a radio-active isotope of nitrogen is obtained by the impact of α -particles on boron.

Shortly after the publication of this discovery it was reported both in England and in the United States that artificial radio-activity could also be obtained by bombarding certain light elements, e.g. carbon and boron, with either protons or deuterons, the latter being the more effective. The bombardment of sodium, in the form of sodium chloride, gives a radio-active form of the same element; this has a half-life period of over fifteen hours, and it has been produced in amounts having activity comparable with that of the natural radio-elements. Radio-sodium obtained in this way appears likely to become a substitute for radium and its allied elements for many purposes.

It may be recorded, in concluding, that in 1934 Professor E. Fermi, of the University of Rome, and his collaborators announced a new type of artificial radio-activity resulting from the bombardment of relatively heavy elements, from aluminium to uranium, by means of neutrons; the effect appears to be fairly general as it has been shown definitely by forty out of sixty elements studied. During the course of the neutron bombardment there is an emission of protons, occasionally of α -particles, and sometimes of neither, but when the source of neutrons is removed a definite β -ray (negative electron) activity, accompanied in some cases by γ -rays, continues with half-life periods varying for different elements from about nine seconds to roughly two days. In a number of instances the radio-elements produced in the bombardment were identified by their chemical properties as being isotopic with the common forms of known elements; for example, phosphorus was shown to produce a radio-active form of silicon, thus:



followed by the disintegration with the emission of electrons:



In this particular instance, a proton having being emitted during the neutron bombardment, the final product is identical with the element initially bombarded, but this is not the case if an α -particle is expelled or if there is no emission at all, as often occurs.

It is interesting to mention that as a result of bombarding the element uranium, which is the heaviest known element, of atomic number 92, evidence was obtained leading Professor Fermi to suggest that he had succeeded in producing the hitherto unknown still heavier element, number 93. Some doubt has been cast on this suggestion, but the arguments are by no means conclusive and this remarkably interesting possibility still remains open.

We are now in a position to consider such questions as the structure of the nuclei of atoms and the evolution of the elements, the latter question in particular being one which has frequently attracted the interest of chemists and philosophers. From the observations made on the discharge of electricity through gases, from studies of radio-activity and of artificial disintegration and transmutation, it is evident that there is an essential unity of all matter: this is no modern idea, but the discoveries of the past few years have supplied material which provides a more firm foundation than the old, as a basis for the discussions.

The ancient Greek philosophers might conceive systems of the universe, based on ideas of motion or of matter, but as their actual knowledge of nature was both limited to mere observation and the results of observation often mistaken and always very imperfect, their theories had no secure foundation. And even down to the comparatively modern times of the eighteenth century philosophical writers, Kant and Leibnitz and Laplace, there was little to consolidate or support conclusions as to the origin of matter and the cosmos. But through all the preceding centuries it is remarkable how frequently the idea of an original primal stuff, called by Aristotle $\nu\lambda\eta$, appears in the works of philosophical writers. When, however, the definite discoveries in chemistry made in the latter half of the eighteenth century, and when the properties of hydrogen, especially its lightness, became familiar it appeared to many chemists of that day as though some of the speculations of the ancients were likely to be fulfilled.

The first, the crudest, and yet one of the most famous of the

modern forms of this idea is what appears in chemical literature as "Prout's Hypothesis." William Prout was a physician and chemist who lived from 1785 to 1850. He held the view that the atomic weights of all the elements are integral multiples of the atomic weight of hydrogen and he says in one of his essays : "We may almost consider the $\pi\rho\acute{o}\tau\eta\ \iota\lambda\eta$ ¹ of the ancients to be realised in hydrogen, an opinion, by the way, not altogether new."

With the more accurate determination of atomic weights during the latter part of the nineteenth century it became evident that atomic weights were not whole numbers, and Stas, who was one of the pioneers of the accurate work of this type, wrote in 1865 : "Je termine donc en disant . . . on doit considérer la loi de Prout comme une pure illusion." Nevertheless many atomic weights were actually found to be nearly whole numbers, more than mere chance alone would have led one to expect, and Stas realised that the subject called for further investigation and is reported to have said : "Il faut croire qu'il y a quelque chose la-dessous."²

It is probably true to say that most chemists had at the back of their minds the feeling that there was something in Prout's hypothesis but the fractional atomic weights proved a serious stumbling-block until the work of Aston on isotopes began to appear from 1920 onwards (see chapter VII). His results have shown that when the atomic weight of an element departs appreciably from a whole number, as in the well established case of chlorine, for example, whose atomic weight is 35.457, it consists of a mixture of isotopes with atomic weights *very close to whole numbers*, thus 34.98 and 36.98 for chlorine. *Of the large number of elements so far examined in no case has the atomic weight of any isotope been found to differ from a whole number by more than 0.1*, and in many cases the difference is much less. Between the atomic weights of 1 and 210 only eight places have not been so far filled by any stable isotope, and there still remain four elements to be studied, so that it is unlikely that more than four vacancies will remain.

These facts render it highly probable that the nuclei of all elements, wherein the mass is centred, are made up ultimately of particles having a mass equal, or very close, to unity; the

¹ Referred to as "protyle" in English.

² Stas Memorial Lecture by Professor J. W. Mallet, *Journal of the Chemical Society*, 1893, p. 1.

particles satisfying this requirement are, of course, protons and neutrons, and these appear to be the fundamental units of all nuclei. It is possible that a proton may prove to consist of a neutron and a positron, or a neutron may be made up of a proton and an electron, but for the present it is sufficient and satisfactory to regard the protons and neutrons as independent fundamental units of nuclear structure. In view of the emission of α -particles from the nucleus in radio-active changes and in certain cases of bombardment already mentioned, and the stability of nuclei having masses which are multiples of four, it appears probable that four unit particles, two protons and two neutrons, combine to form a secondary, relatively stable, unit of mass 4 and carrying two charges, which is, of course, the α -particle.

Since β -particles (electrons) are often expelled in radio-active changes it was at one time thought that all nuclei contained free electrons in addition to protons—neutrons were not then known—but this view presents certain mathematical difficulties, and increasing support is being obtained for the idea that no electrons are present in atomic nuclei. In order to account for β -ray activity it is suggested that the process :



occurs, but in order to satisfy exact energy and mass requirements it is necessary to postulate the existence of a new particle, called a *neutrino* by Fermi, which has no charge and a mass about the same as that of an electron. So far no experimental evidence for this particle has been obtained, and in view of its supposed properties it is hardly likely that it will be detected easily, even if it does exist.

According to the suggestion that nuclei consist of neutrons and protons only, the difference between isotopes, since they have the same positive nuclear charge but differ in mass, is to be attributed to a difference in the number of neutrons, the number of protons being the same in each case. For example, the nucleus of the isotope of chlorine of mass 35 would consist of 17 protons and 18 neutrons, whereas the isotope of mass 37 would be made up of the same number of protons and 20 neutrons. The total masses would thus be 35 and 37, respectively, and the nuclear positive charge, and hence atomic number, would be 17 in each case.

We must enquire next into the relationship between the masses

of the atoms and the masses of the units from which they are constituted ; consider the case of helium, for example, the atomic weight being 4.0022. Suppose its nucleus consists of two neutrons, each of mass 1.0067 and two protons of mass 1.0072, and there are in addition two orbital electrons, each contributing 0.00055 to the mass, the total will be 4.0289. In the formation of helium, therefore, there is a loss of mass, called the "mass defect," of $4.0289 - 4.0022 = 0.0267$, which represents the energy released in the formation of the helium atom. By Einstein's theory of relativity the energy equivalent of this mass defect can be calculated and is found to be about 800,000 kilowatt-hours for the formation of four grams of helium ! If, therefore, we could make the necessary protons and neutrons combine to form helium we should liberate this stupendous amount of energy. The mass defect is found with all elements, but unfortunately there is no method known for causing simple atoms to unite to form complex ones, although according to Professor R. A. Millikan, of California, such union is actually taking place spontaneously in inter-stellar space.

In many of the disintegration and transformation processes already described appreciable mass defects occur : for example, in the disintegration of lithium nuclei into α -particles, by the impact of swift protons, observed by Cockroft and Walton, there is a mass defect of 0.015, which means that for every gram of lithium disintegrated as much as 60,000 kilowatt-hours of energy are liberated. In actual practice so few protons are effective and so few atoms of lithium are actually hit and disrupted, that the total amount of energy resulting from the loss of mass is only very small indeed, in fact much smaller than that used to make the protons move with the necessary high velocity to cause disruption. If in some way this process could be made more efficient we should have a means of tapping the energy of the atom, and so realising the dreams of engineers and physicists from the commencement of the present century. The prospects of the realisation of this achievement are not, however, very promising.

In concluding this chapter a word may be said about the genesis of the elements : there has been much discussion of this subject in recent times, but opinion still remains divided. Since all matter is believed to be composed of protons, neutrons, and electrons, with α -particles as secondary units, it is easy to picture

the gradual building up of more and more complex atoms, although it is by no means easy to say *how* the process occurs. Professor Millikan is of the opinion that in the depths of space simple elements are uniting to form heavier ones, and the energy resulting from the consequent loss of mass is the source of the highly penetrating "cosmic rays" which he discovered. Sir Arthur Eddington and Sir James Jeans, in England, dissent from this view, however, and suppose that in general the universe as we know it is running down and not being built up. If this is the case it would appear to be futile for us to speculate concerning the conditions and the means whereby the elements attained the state of complexity before the simplification process commenced: nevertheless the problem remains, though it appears to be one for the philosopher rather than for the chemist!

CHAPTER IX

SOLUTIONS

PROBABLY few persons as they drop the sugar into a cup of tea concern themselves with the problem which is presented by the disappearance of the lump and the fact that in a few minutes, even without stirring, the taste of the sugar can be recognised in every part of the liquid. Suppose the sugar to be immersed in water the change can be watched more readily, and it is at once seen that the crystalline mass falls quickly asunder, while a dense syrupy liquid streams away from it. After a time, if sugar is added in successive portions to the same quantity of water, the process of dissolution slackens, the lumps crumble away less rapidly, and ultimately they undergo no change, the liquid being then, to use the common expression, saturated.

But every cook knows that if heat is applied and the temperature of the liquid raised more sugar will dissolve until another point of saturation is reached as the liquid boils. If such a liquid is then allowed to cool to the temperature of the air a portion of the sugar soon begins to separate from the liquid in the form of crystals the size of which depends on the volume

of liquid and the condition whether it is stirred about or left at rest.

A lump of white marble looks to the unaided eye so much like loaf sugar that it might easily be mistaken for that substance, but if a lump of white marble is placed in hot tea or cold water no change would be observed ; it would not dissolve. But now suppose that the lump of white marble is immersed in water to which some nitric or hydrochloric acid has been added, there will be a great effervescence, bubbles of gas (carbon dioxide) escape, and the marble rapidly disappears, forming a clear colourless solution. This solution, however, contains something different from marble, and if the liquid is duly concentrated it will yield crystals, quite unlike marble, which consist of the nitrate or chloride of calcium, containing also a certain proportion of water. The case of sugar in water differs from that of marble in acid, therefore, in the fundamental fact that the sugar can be recovered unchanged in properties, while the marble cannot be recovered from the liquid because a chemical change has taken place, and part of its components has been lost.

Why does the sugar dissolve in water while the marble does not dissolve except on condition of undergoing chemical change ? These are questions to which the physicist and chemist can give as yet only partial and imperfect answers. We may try to follow in imagination the change in the sugar. First we must recall the fact that the molecules of gases are free from each other and every one, according to the kinetic theory, moves about rapidly and independently of the rest, only knocking up against them and continually altering the direction of its course. In liquids we must believe, from the phenomena of diffusion, that something of the same kind is continually going on with this important difference, that there are relatively few separate and independent single molecules. A large proportion of the molecules move together in clusters or companies, which are larger at low temperatures and smaller if the temperature is raised. Thus the molecule of water in the state of gas, that is superheated steam, consists of two atoms of hydrogen and one atom of oxygen, or expressed in symbols H_2O . In the liquid state at the common temperature of the air these join together or at any rate move together in parties of two or more molecules, such as $(H_2O)_2$, $(H_2O)_3$, etc.

A minute quantity of the compound is also probably in a state of dissociation, being resolved into ions H and HO. This will be explained later and does not concern for the moment the consideration of the question relating to sugar. We must suppose then that a crystal of sugar immersed in water is exposed to a shower of blows from the moving molecules of the water which are sufficiently strong to detach separate molecules of the sugar from the surface and cause them to move about in the liquid in the same manner as molecules of the solvent itself. They are thus made to behave as they would do if converted into gas by the application of heat. Sugar cannot be gasified in this way because its atoms separate from each other and form new combinations, that is chemical decomposition takes place, before the necessary temperature is reached.

Why the molecules of calcium carbonate are not separable from one another in a similar way by the action of water may be explained by saying that the cohesion between them is greater than the cohesion between molecules of sugar. That, however, is merely a word and not an explanation, and serves as an admission of ignorance as to the nature of the difference between the two substances.

Sugar dissolved in water is then assumed to be in a condition comparable with that of a gas, only the spaces between the molecules are occupied by moving molecules of another kind. The molecules of gases exert pressure which is regulated by temperature, and the number of molecules in a given volume conforms to the law of Avogadro. In the solution of sugar an analogous condition prevails. The boundary of a mass of liquid is determined by what is called "surface tension," which acts in such a way that the liquid, at any temperature much below its boiling-point, behaves as though it were confined within an elastic skin which always tends to squeeze it into the smallest possible space. This is shown by the spheroidal form of detached drops. Within this bounding surface the sugar and the water exert a pressure which is called the "osmotic pressure." The earliest observations of this pressure and measurements of it were made by Pfeffer, professor of botany at Bâle, nearly sixty years ago. But the interpretation of his results led the Dutch professor Van 't Hoff,¹ in 1887, to formulate the theory of solution which

¹ Jacobus Henricus van 't Hoff was born in Rotterdam on August 30th, 1852; he studied at the Polytechnic Institute at Delft, and at the Universities of

has just been briefly explained. Van 't Hoff found from Pfeffer's measurements the existence of a complete parallelism between the osmotic pressure of a dissolved substance and the laws which govern gas pressures.

In the first place the osmotic pressure, at any rate in dilute solutions, is in direct proportion to the strength of the solution, that is, to the amount of dissolved substance in unit volume of the liquid, and this is equivalent to saying that the osmotic pressure is inversely proportional to the volume, which is one form of Boyle's Law.

The following figures show some of the results of Pfeffer's work :

SUGAR IN WATER				
Percentage of sugar, C.		Osmotic pressure P in mm. of mercury.		$\frac{P}{C}$
1	..	535	..	535
2	..	1016	..	508
2.74	..	1513	..	554
4	..	2082	..	521
6	..	3075	..	513

It is evident in this case that, allowing for reasonable experimental errors, the osmotic pressure is in the case of sugar directly proportional to the amount of dissolved substance per unit volume.

Pfeffer also found that osmotic pressure increases with temperature and that the increase is in harmony with Gay Lussac's

Leyden and Utrecht ; he also spent some time in Bonn and Paris. In 1876 he became Lecturer in Physics at the Veterinary School of Utrecht, and two years later was appointed Professor of Chemistry, Mineralogy and Geology at Amsterdam. Because of his fame as a scientist van 't Hoff was offered a Professorship in the Prussian Academy of Sciences, at Berlin ; this post he accepted as it involved no teaching duties and gave him ample facilities for research. He was presented with the Davy Medal of the Royal Society in 1893, and elected a Foreign Member in 1897 ; in 1903 he was awarded the Nobel Prize for Chemistry. Van 't Hoff died at Stieglitz, in Germany, on March 11th, 1911. He made a number of very important contributions to physical chemistry : amongst these may be mentioned his work on thermodynamics and the concept of chemical affinity, the theory of dilute solutions, and the study of the oceanic salt deposits, such as those at Strassfurt, in Saxony. Mention must also be made of the theory of the tetrahedral carbon atom which van 't Hoff put forward in 1884 ; this is referred to in the chapter on Valency and Stereochemistry. In conjunction with Professor Wilhelm Ostwald he founded the *Zeitschrift für Physikalische Chemie*, the most important physico-chemical journal, in 1887.

law for gases, which states that the volume of a gas is directly proportional to the absolute temperature.

Further, when solutions containing different substances of the same chemical character are compared together and the quantities of the different substances are in the proportion of their *molecular weights*¹ dissolved in equal volumes of the same solvent, they exert the same osmotic pressure. This is parallel with the law of Avogadro. The qualification here mentioned must, however, be observed, that is, sugars, alcohols, and neutral substances generally which are not electrolytes may be compared together, while acids, bases, salts may be compared together, but for reasons to be explained presently the osmotic pressures given by such substances, which conduct an electric current, and are decomposed by it, are not comparable with those of substances like sugar. Their osmotic pressures are in general much greater.

Pfeffer's method of experiment was based on the employment of a membrane which allows water to pass through, but which does not allow the dissolved substance, such as sugar, to pass. If now we imagine a small vessel composed of this *semipermeable* material, filled completely with a solution of sugar and connected with a manometer, any change in volume of the liquid will be indicated by the manometer. If the semipermeable vessel is then immersed in pure water an increase of pressure soon begins to be manifest by the movement of the mercury in the manometer, and this is due to the passage of water from without inwards through the membrane. The maximum pressure indicated by the manometer is the osmotic pressure. Pfeffer's methods have been improved upon in more recent years, and measurements have been made by Morse and Frazer in America up to 20 atmospheres and more; by means of a special apparatus devised by Lord Berkeley and Mr. Hartley, pressures have been recorded for strong sugar solutions up to more than 100 atmospheres.

The nature of the membranes which have been used is a matter of interest on account of physiological considerations. The material most commonly used in the earlier experiments was a film of copper ferrocyanide, which is formed when a drop of

¹ The molecular weight, or more strictly the "gram molecular weight" is the weight, expressed in grams, obtained by adding together the atomic weights of all the atoms contained in the molecule.

solution of copper sulphate is brought into contact with a solution of potassium ferrocyanide, but measurement of pressures only becomes possible when this material is deposited in the pores of unglazed china-ware, of which the experimental vessel to hold the solution is made. Through this material water passes freely, but neither copper sulphate nor potassium ferrocyanide, common sugar nor dextrose. Other artificial membranes have been prepared for use in the experimental study of the phenomena, but there are many interesting cases of natural membranes, of which one has been carefully studied by Professor Adrian Brown within recent years. He finds that the barley grain is covered with a membrane of this kind, which, so long as the seed is uninjured, allows water from any solution in which it is immersed to pass into the interior of the grain, but it completely excludes sulphuric acid, common salt, and many other substances. And even grains which have been boiled in water so as to destroy their vitality retain this selective power, and thus show that this power is due to a physical property of the membrane and is not a physiological effect of living matter. The importance of discoveries of this kind is obvious in connection with the changes which go on in both vegetable and animal tissues. There must be many different semipermeable membranes existent in such tissues to account for the remarkable and rapid exchanges between fluids contained in adjacent cells. To cite one instance the ascent of the sap from the root to the stem and often distant branches of a tree must be dependent on action of this kind in which water passes freely, while the soluble contents of the cells forming the wood and leaf are not suffered to be lost or washed away by rain.

If the principle is accepted that different substances taken in the proportions of their molecular weights in equal volumes of the solution have the same osmotic pressure, it is obvious that by the determination of the osmotic pressure a method is provided for the determination of molecular weight. But the experimental determination of osmotic pressure is not an easy matter, and it is therefore more practicable to use for comparison a solution of known osmotic pressure. Liquids which have the same osmotic pressure are usually described as *isotonic*, and the comparison may be made by observing whether or not water passes from the solution to be tested into the standard solution contained in a natural or artificial cell membrane.

It is unnecessary in this place to pursue the subject further, especially as it is treated very fully in all the textbooks on physical chemistry. Enough, however, has been said to show that the physics and chemistry of a cup of tea are more complicated than is perhaps commonly supposed.

The subject, however, is by no means exhausted. There is reason to believe that in the act of dissolution in a liquid many substances unite chemically with a portion of the solvent. Evidence of this is derived from the fact that heat is evolved when many substances are placed in contact with a liquid capable of dissolving them, the evolution of heat being a common sign of chemical union.

In many cases also changes of colour are observed, and when, from the resulting solution, crystals are deposited, these crystals contain definite molecular proportions of water or alcohol or other liquid, in the midst of which they have been formed. An example may be found in the crystals of common washing soda, which is represented by the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. If some of these crystals placed in a saucer are gently heated they melt easily and soon give off steam. After a time the liquid dries up to a white powder which consists of the soda without the water. If the dry powder is now allowed to become quite cold and an equal weight of cold water is poured on it the mass becomes hot, and no solution is produced, for the water unites with the salt to reproduce the original substance. If more water is now added the salt passes again into solution, and after some time, if too much water has not been added, crystals appear having the same composition and properties as the original washing soda. In most cases the solubility of a salt in water is, like that of sugar, continuously greater with rise of temperature up to the boiling-point of the solution or even much beyond that point. But this is not always the case. Glauber's salt (sodium sulphate) is an excellent example. If some of this salt, which is sold in small crystals for medicinal use, is mixed with less than its own weight of water and very gently warmed it dissolves freely, forming a clear solution. If the latter is then heated to the boiling-point a shower of small crystals will be observed falling within the solution, and these crystals consist of sodium sulphate, Na_2SO_4 , in the anhydrous state, that is, without combined water. The crystals of Glauber's salt contain ten molecules of water, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and the solubility of these increases with rise

This subject is so important and has of late years occupied so much of the attention of chemists that it deserves a somewhat close consideration.

Electricity has long been known to be capable of passing through matter in two ways. Metals, and some other bodies in a less degree, allow a current to pass through them with comparatively little loss. They are called "conductors," and silver and copper are among the best conductors, while platinum, tin, and lead are less good. When a metal like platinum or a non-metal such as carbon, as in the older types of electric lamp, is used to carry a current of electricity a part of the energy disappears as electricity, and appears as heat, but no chemical change is produced. On the other hand, if a current is passed through a solution of an acid, a base, or a salt the compound is resolved into two parts which are liberated at the opposite poles or electrodes. Such substances are called "electrolytes." Sugar, alcohol, and neutral substances generally, such as chloroform, ether, etc., are not electrolytes, and offer great resistance to the current. The older theory of electrolysis assumed that the two components of the electrolyte were torn from each other by the force of the current. According to the modern doctrine, on the other hand, the assumption is that the separation of the ions¹ begins, and in all cases of good electrolytes is carried to a con-

¹ The term *ion*, from the Greek, meaning "wanderer," was first introduced by Faraday; it is used for the electrically charged particles which carry the electric current through an electrolyte (see p. 184).

siderable extent *when the electrolyte is dissolved* in water or other appropriate liquid. Take the case of common salt for example ; when dissolved in water this theory requires us to suppose that a considerable proportion of the salt is no longer sodium chloride.¹ It is believed on the contrary that most of the molecules are broken up into ions of positive sodium, represented by the symbol Na^+ , and ions of negative chlorine, Cl^- . These ions move about in the liquid as independent particles, their freedom of movement being complete in every sense but one. Any attempt to remove one kind of ion is fruitless, for if the liquid is evaporated and crystallisation of solid salt ensues the positive and negative ions unite to reproduce molecules of the ordinary neutral kind. And when a current is passed through the liquid for every positive ion removed at one electrode a negative is withdrawn at the other.

If a solution of common salt is placed in a porous pot or bag of parchment paper which is immersed in pure water, a portion of the salt will diffuse into the water. It is an eminently good diffuser, as compared with sugar and especially with gum or albumen, all of which move in a similar way, but far more slowly. But the salt which passes through to the water as the result of this spontaneous movement consists of sodium ions and chlorine ions in exactly the same proportions as in the salt which remains behind, so far as chemical analysis can determine. No doubt, as will be mentioned presently, all sorts of ions do not move about at the same rate, some being very much faster than others, but there are electrostatic forces at work between the positive and negative particles which prevent them from wandering beyond the range of each other's attraction, and thus becoming separable to anything more than an almost infinitesimal extent far beyond recognition by chemical analysis. There is in fact no reason to suppose that it will ever be possible to separate a neutral salt solution into a positive portion and a negative portion. There may be membranes in animal and vegetable tissues which possess to a small extent this kind of semipermeable property, but very little is definitely known in this direction. At the same time it is possible that some of the electrical effects observed in leaves and other living parts may be traced to this

¹ According to modern views (see p. 189) the solid crystal of sodium chloride actually consists of ions held together by forces of electrical attraction.

cause. Evidence of the existence of free ions is obtained from other considerations.

If this hypothesis is adopted it will be apparent why salts in general exert an osmotic pressure so much greater than that which is observed in the case of sugar. Each molecule of salt splits up into two or more ions, each of which has the same osmotic effect as an ordinary molecule; a solution made up from a gram molecular weight of potassium nitrate, KNO_3 , each molecule of which yields two ions, will have almost twice the osmotic pressure of a solution containing a gram molecular weight of a non-ionisable substance like sugar.

When a substance of any kind is dissolved in, say, water the properties of the liquid are modified. Thus it is a matter of common knowledge that sea water does not freeze so easily as fresh water, and the practice is familiar of strewing salt on a frozen surface to induce thaw, that is to form a liquid which remains liquid, while water at the same temperature is ice. It may not be so commonly known that the boiling-point of water is raised many degrees by the addition of common salt, but this is familiar to the practical chemist, who makes use of the fact when he requires a bath for experimental purposes somewhat hotter than boiling water.

About 1883 the first tolerably accurate estimations of the effect of dissolved substances in lowering the freezing-point of water were published by the late Professor Raoult of Grenoble. It was previously known that a determinate quantity of the same substance dissolved in the same quantity of water always reduced the freezing-point by the same number of degrees, and that when equal quantities of different substances were dissolved there was a simple relation of some kind among their molecular weights. But it was only after a long series of experiments that Raoult succeeded in establishing his important generalisations.

When known quantities of the same substance are successively dissolved in the same portion of a solvent on which it has no chemical action, there is a progressive lowering of the freezing-point of the solution, which is proportional to the weight of substance dissolved in a constant weight of the solvent. But it is not possible to carry the process very far, as deviations from this rule occur when strong solutions are used. But the relation of the depression produced by a small quantity of the substance

to its molecular weight enabled Raoult to arrive at an important conclusion. The following are some of his experimental results :

Name of dissolved substance.	Molecular weight.	Depression of freezing-point by 1 gram of substance in 100 gr. water.	Product of depression and molecular weight.
Methyl alcohol . .	32	0.541	17.3
Ethyl alcohol . .	46	0.376	17.3
Butyl alcohol . .	74	0.232	17.2
Glycerine . .	92	0.186	17.1
Mannite . .	182	0.099	18.0
Invert Sugar . .	180	0.107	19.3
Milk Sugar . .	360	0.050	18.1
Cane Sugar . .	342	0.054	18.5
Salicine . .	286	0.060	17.2
Phenol . .	94	0.165	15.5
Pyrogallol . .	126	0.129	16.3
Acetone . .	58	0.294	17.1
Ether . .	74	0.224	16.6
Ethyl acetate . .	88	0.202	17.8
Acetamide . .	59	0.301	17.8
Urea . .	60	0.286	17.2
Ammonia . .	17	1.117	19.9
Ethylamine . .	45	0.411	18.5

A glance at these figures is sufficient to show that the depression produced by 1 gram of the substance is inversely as the molecular weight, and hence that the product of the two is a constant. Of course the product varies a little owing to experimental difficulties, but the rule has been since well established by the results of hundreds of experiments made by other chemists in laboratories all over the world. And in fact determinations of molecular weights by observation of the freezing-point, of solutions is now one of the commonest and most useful operations in the course of research into the composition and character of new compounds of all kinds.

Suppose the weight W in grams of such a substance as sugar is dissolved in 100 grams of water and the number of degrees below 0° at which the solution begins to freeze be expressed by C .

Then $\frac{C}{W}$ will represent the depression which would be produced by 1 gram of substance dissolved in 100 grams of water. If this expression is multiplied by the molecular weight of the substance dissolved, in this case sugar, the product is the depression which would be theoretically produced by the molecular weight M in grams of sugar dissolved in 100 grams of the solvent. This molecular depression may be expressed by K , and is equal to $\frac{C}{W} \times M$.

When different substances of the same neutral character as sugar are dissolved in the same solvent the value of K is found to be the same. Hence a method is provided whereby if K is known for the solvent chosen, and for compounds analogous to the one under investigation, the molecular weight of the latter can be determined, or rather, from the possible molecular weights that value is chosen which comes nearest to the value of M in the formula $M = \frac{W \times K}{C}$. The solvents most commonly used are

water, acetic acid, and benzene, for which the values of K now adopted are approximately 19, 39, and 51.

The method outlined here is the most accurate and the most commonly used method for determining the molecular weight of soluble substances which are not volatile without decomposition and of which the vapour density cannot therefore be determined.

The apparatus used in such work is described in all the best text-books, where also an account will be found of the method based on the observation of the boiling-points of solutions. The latter method is a little more difficult to carry out, and is not so commonly resorted to as the freezing process. Obviously the boiling-point of a liquid is directly related to its vapour pressure, for a liquid boils when the pressure of the vapour produced just exceeds the pressure of the atmosphere on the surface. Consequently a method is occasionally used which consists in observing the change in the vapour pressure of the solvent at a fixed temperature when a known quantity of a substance is dissolved in it. And by another formula based on Raoult's work the molecular weight of the dissolved substance can be determined. The rules relating to the vapour pressures of dilute solutions are similar to those relating to freezing-points.

An important point in regard to these practical experimental

methods is the relation in which they all stand to osmotic pressure, for molecular proportions of different substances when dissolved in the same quantity of the same solvent exert equal osmotic pressures, and raise the boiling-point or lower the freezing-point and the vapour pressure to the same extent. These effects are dependent on the number of particles present without regard to their composition.

Many other problems connected with solutions might be discussed if space permitted. The application of the process of dialysis or selective diffusion of dissolved substances discovered by Graham more than half a century ago has been utilised in the extraction of sugar from the beet.

Sugar beet contains 14 to 18 per cent of cane sugar together with a variety of other substances such as vegetable acids, asparagine and albuminous matter. In order to separate the sugar as much as possible from these substances, which if expressed along with it would interfere with its crystallisation when the juice is evaporated, the beet roots after being washed are cut into very thin slices, which are laid in warm water. During its immersion a process of dialysis goes on, each cell of which the tissue consists acting as a membranous bag through which the sugar and any salts present pass pretty rapidly, while the non-crystalline albuminous and gummy matters remain behind. A series of tanks is employed into which the water is pumped in regular order so that the fresh water is added to the already partly exhausted pulp, while the extract is passed on to the tanks containing fresh beet, and so a fairly concentrated solution of sugar is ultimately obtained. This solution is then treated with lime and afterwards with carbon dioxide or sulphur dioxide gas.

The insoluble precipitate, which contains a considerable amount of organic matter, is then passed through a filter press, and the clear liquid evaporated in vacuum pans till it begins to crystallise. This method of extraction, by taking advantage of the process of diffusion, is indispensable and could not be replaced without great disadvantage by any process of extracting the juice by pressure.

The study of aqueous solutions has also been applied to the elucidation of problems connected with the formation of mineral deposits. The ocean is the recipient of all the very numerous substances washed out of the land by the action of rain, and the

consequent delivery of these substances by streams and rivers into the sea. From the sea the water evaporates and passes invisibly into the atmosphere, but there can be no return of the dissolved salts to the land except in the form of spray carried by the wind. In countries like England with an extensive coast the amount of salt thus returned is considerable, as fine spray is carried by strong winds a long distance inland.

Deposits of rock salt have been formed by slow evaporation of the water of such enclosed basins as the Great Salt Lake in Utah, the Dead Sea, etc., into which streams bring soluble matter and from which there is no exit. The consequence of these conditions is that in the course of ages such water becomes highly saline and deposits are formed at the bottom and round the shores of such lakes. Naturally the salts which are least soluble in water are deposited first if they are present in appreciable quantities. Thus a bed of gypsum (hydrated calcium sulphate) is usually present below deposits of rock salt, but as salts of potassium and magnesium, partly in the form of sulphate, are associated with the sodium chloride the products may be very numerous. A very important research was undertaken a few years ago on the formation of oceanic salt deposits by Professor Van 't Hoff, and carried on by him with the aid of his students for many years, till shortly before his death in 1911. This had special reference to the famous salt deposits at Stassfurt in Prussia, from which supplies of potassium and magnesium salts have been distributed in large quantities during many years past, and the lack of which has caused some inconvenience outside Germany during the war. The salts from Stassfurt which have become familiar in commerce are :

Carnallite	.	.	.	KCl, MgCl ₂ , 6 H ₂ O,
Kainite	.	.	.	KCl, MgSO ₄ , 3 H ₂ O,
Kieserite	.	.	.	MgSO ₄ , H ₂ O,
Sylvite	.	.	.	KCl.

There are many other double salts in these deposits, but the result of Van 't Hoff's work has been to explain how it came about that these compounds were formed and in what order. Temperature has a good deal to do with it, but pressure is also a condition which may modify the composition of some of the salts in the solid state as they occur in the veins under-ground.

In addition to explaining how these various salts were formed

there is the practical problem of finding means of separating the useful compounds, such as potassium chloride, from the complex mixtures found at Stassfurt and from those deposited in salt lakes such as the Dead Sea and Searles Lake in California. In this work studies of solution are involved, and the chemist has to find the conditions under which a particular salt will separate out in the solid form, whereas the other constituents of the mixture remain in solution.

Another important question which has been studied within recent years is that which relates to the formation of the double carbonate of magnesium and calcium which constitutes the mineral called *dolomite*, which is so abundant as to form whole mountains in some parts of the world, the Eastern Alps for example. The substitution of magnesium carbonate for calcium carbonate in such rocks is the problem which has occupied chemical geologists without the discovery of a definite answer in each case. The examination and analysis of the core obtained from a bore hole drilled into the atoll of Funafuti led Professor Judd in 1904 to the conclusion that the original calcium carbonate, secreted by the corals, has been partly replaced by magnesium carbonate after the death of the organisms. While the proportion of magnesium carbonate near the surface is from 12 to 16 per cent, at a depth of 637 to 1114 feet, it increases and is maintained with some variations at 40 per cent, a proportion which approaches the amount required (45-65) to form dolomite. The true explanation of this change is yet to be sought, but a further attack on the problem, with the aid of the knowledge acquired by a study of Van 't Hoff's researches, is much to be desired, and would probably lead to interesting results.

CHAPTER X

ELECTROLYSIS

It is little more than a hundred years since the decomposition of water by an electric current was first seen by Nicholson and Carlisle. A few years later Davy, making use of the same agency, isolated potassium and sodium, and with the aid of a battery consisting of 2000 plates first showed to an audience at the

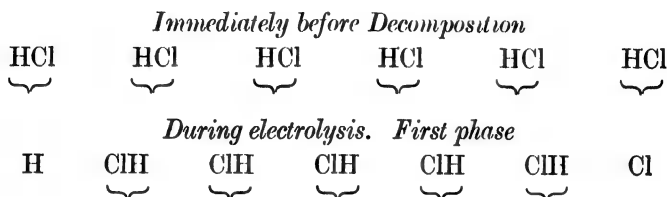
Royal Institution the arc light between points of charcoal. Faraday succeeded Davy, and within ten years after the death of the latter the quantitative laws, relating to electro-chemical decomposition, were established by him. The electric deposition of metals from solution is the basis of the beautiful art which gives to every household its silver and chromium plated articles, and supplies the means of copying with the most minute detail any surface which is, or can be rendered, conductive of electricity. Since the days thus briefly referred to the means of generating electric currents have developed chiefly out of the discoveries of Faraday. The application of the current to the production of heat or motion is familiar but cannot be further described at this point. The question which has occupied chemists for a hundred years is what is the nature of the process of electrolysis ; why does the electric current so easily decompose a solution of common salt or acidified water, while it has scarcely any effect on a solution of pure sugar or alcohol ?

Around questions like these an active discussion has raged for more than fifty years, and though practical unanimity on the main part of the modern theory has been reached, many accessory questions have yet to be settled and probably will remain unsolved for many years to come.

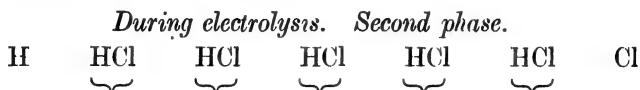
First of all it will be useful to recall the hypothesis which was accepted for the greater part of the nineteenth century. It will be the easier to perceive the profound nature of the change which has been introduced. Imagine, for example, that a solution of hydrochloric acid is submitted to the action of a current. If the solution is moderately strong hydrogen gas is evolved from one pole, and chlorine gas from the other.¹ These two substances Faraday called the "ions" of hydrochloric acid. According to the older hypothesis introduced by Grotthuss in 1805 it was supposed that throughout the liquid, between the poles or electrodes while in action, the molecules were ranged in a series of polar chains, the positive constituent, in this case the hydrogen, facing in one direction toward the negative plate or cathode, while the negative constituent, in this case chlorine, was drawn toward the positive plate or anode. In the process of electrolysis the positive hydrogen atoms moved from molecule to molecule along the chain until at the end, at the surface of the cathode, they were attracted away and then appeared in the

¹ If the solution is dilute then oxygen is obtained instead of chlorine.

free state in the form of hydrogen gas. The negative atoms of chlorine were supposed to move in a similar manner along the chain in the opposite direction. This may be represented in the following diagram :



In order to explain the continuance of the process it is then necessary to assume that the new molecules turn round so that their ions face the electrodes to which they then move.



According to this idea the effect of the current is first to cause all the molecules between the electrodes to arrange themselves in lines having the ionic constituents facing in opposite directions. This would appear to involve the setting up of a peculiar structure or at least a tactical arrangement of the particles in the liquid which should have some effect on its optical or other properties. Nothing of the kind can, however, be detected in the space occupied by the liquid between the electrodes. Secondly, the theory assumes that the molecules of the electrolyte, though moving about in the liquid, are all complete and entire until the moment when the electro-motive force is applied, and that then, and not sooner, they are separated by the opposite electrical attraction of the cathode and anode respectively.

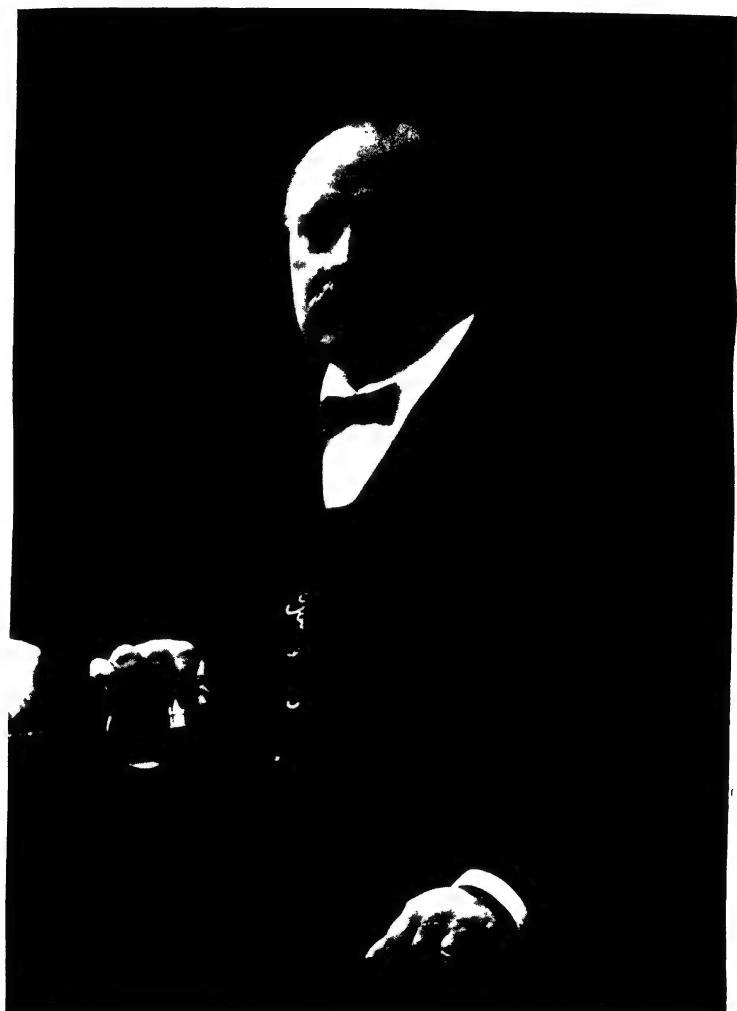
In such operations if the same current passes successively through solutions of different electrolytes the quantities of substance liberated at each pole is in proportion to the chemical equivalents of these substances. That is if 1 part by weight of hydrogen is liberated in the cell charged with hydrochloric acid, 108 parts of silver would be deposited from a solution of a silver salt included in the same circuit. Similarly $32\frac{1}{2}$ parts of zinc, $103\frac{1}{2}$ parts of lead, $31\frac{3}{4}$ parts of copper would be liberated for 1 part of hydrogen. At the anode where the chlorine appears

for every $35\frac{1}{2}$ parts of that element set free, 8 parts of oxygen, or 80 parts of bromine, or 49 parts of sulphuric acid would appear at the same surface. This is in accordance with Faraday's law. It appears that all soluble or fusible compounds are decomposed by the same current in chemically equivalent quantities, however different they may be in chemical constitution. It is also a fact that the smallest current sent through an electrolyte produces chemical decomposition in proportion to its strength in accordance with Faraday's first law (p. 94). If molecules, in the fluid state of a substance, are broken up by the current it might be expected that while some would be easily decomposed, others would be broken up with greater difficulty, and one or other of Faraday's laws would not be valid.

An idea of great importance was introduced into chemistry by the late Professor Alexander Williamson about 1850, in the endeavour to explain the remarkable process by which alcohol and sulphuric acid react to form ether. He says,¹ "We are forced to admit that in an aggregate of molecules of any compound there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH , the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but on the contrary is constantly changing places with other atoms of hydrogen, or what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basylous elements, hydrogen and copper, do not limit their change of place to the circle of the atoms with which they were at first combined,—the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid," and so forth. It is not necessary to quote further, but this view is quite analogous to those held concerning electrolytes at the present day.

The same idea was made use of in 1857 by the German physicist

¹ *Quarterly J. Chem. Soc.*, Vol. IV., p. 111.



Clausius, in order to explain electrolysis, but he could not answer the question as to the proportion of the dissolved substance which must be supposed to be in the act of exchanging constituents, and therefore dissociated into ions. To the late Professor Svante Arrhenius,¹ of Stockholm, we owe the "theory of electrolytic dissociation" which has helped very considerably to systematise our knowledge of the properties of electrolytes; this is the view already expressed (p. 176) that immediately an electrolyte is dissolved in water it splits up (dissociates) to a considerable extent into its constituent positive and negative ions.

In one of his lectures on "Theories of Chemistry," given in 1904, Professor Arrhenius refers to the beginning of his own work on the subject in the following words: "In the year 1883 I carried out an investigation on the conductivities of different electrolytes, and was thereby led to the conclusion that all the molecules of an electrolyte do not conduct the electric current. The molecules were therefore divided into two classes, active and inactive. At high dilutions all the molecules were supposed to be transformed into the active state. The number of electrically active molecules in a solution (e.g. of an acid) was measured by its conductivity.

"Now the order of different acids, as regards their power of

¹ Svante August Arrhenius was born at Upsala, Sweden, on February 19th, 1859; he attended the university in the town of his birth, and after graduating in 1884 he commenced to teach physics there. Between 1886 and 1890 he travelled over Europe and spent some time in the laboratories of famous scientists in Riga, Würzburg, Graz, Amsterdam, and Leipzig; it was during this period that the theory of electrolytic dissociation for which Arrhenius is famous was developed from the somewhat vague ideas put forward in his graduation thesis. In 1891 he was appointed to a lectureship at Stockholm, where he became Professor of Physics in 1895; between 1897 and 1902 he was also Rector of the University. To compensate him for his refusal of a number of attractive offers to leave his native country, Arrhenius was made Director of the newly formed Nobel Institute for Physical Chemistry in 1905; the new laboratories, devoted to research, were inaugurated in 1909, and he presided over them until February, 1927, retiring some eight months before his death on October 2nd, 1927. Arrhenius received many honours from foreign scientific academies; in 1902 he was awarded the Davy Medal of the Royal Society, of which he was elected a Foreign Member in 1911, and in 1914 was the Faraday Medallist of the Chemical Society. He was awarded the Nobel prize for Physics in 1903. Arrhenius not only contributed to physical chemistry, he also wrote extensively on physiological chemistry, immunochemistry, meteorology, and cosmic physics; he was especially interested in philosophical theories of life, and in his latter years devoted some time to the popularising of scientific knowledge. For further details, see Arrhenius Memorial Lecture by Sir James Walker, *Journal of the Chemical Society*, 1928, p. 1380.

displacing one another from their salts, was known from thermochemical measurements. This order was exactly the same as that of the conductivities in equivalent solutions. This circumstance led me to suppose that chemically active molecules are identical with electrically active ones, and therefore the conductivity of an acid was regarded as a measure of its strength. In consequence it was argued that the velocity of a reaction, which may be brought about by different acids, is proportional to the conductivity of the acid used. . . . Generally speaking, there seems to be a certain parallelism between electrical conductivity and chemical reactivity. Gore found that pure anhydrous hydrochloric acid does not (appreciably) attack oxides and carbonates; also it is practically a non-conductor of electricity. Similarly, one can understand why concentrated sulphuric acid may be transported in iron vessels, whereas diluted sulphuric acid attacks them very rapidly."

He then goes on to show that electrolytes differ from non-electrolytes in giving, when in solution, greater osmotic pressures, and greater effect on the freezing, boiling-points, and vapour pressures. This has already been sufficiently explained in the preceding chapter on "Solutions."

Arrhenius subsequently identified the "active" molecules with the free ions present in solution, whereas the "inactive" molecules represented the parts of the electrolyte which had not dissociated into ions. Since the number of electrically active molecules in a solution was believed to be measured by its conductivity, Arrhenius showed how the relative proportions of dissociated and undissociated molecules could be determined from measurements of electrical conductivity; the agreement between the values obtained in this way with those calculated from osmotic pressures, and similar data, was regarded as strong confirmation of the dissociation theory.

Modern developments in chemistry have necessitated some slight modification of the original theory: if electrolytes are divided roughly into strong and weak categories, according to whether they are good or bad conductors, then it can be said the Arrhenius theory applies essentially unchanged to the latter group, namely, the weak electrolytes consisting of the majority of acids and bases. Most salts are strong electrolytes, and the modern view, to which reference will be made later, is that even in the solid state they are made up *entirely of ions* held together by

electrical and other forces. In the crystal the ions are not free to move, but if the solid is melted by heat or by dissolving it in water the ions immediately become free and are able to conduct the electric current. A crystal of sodium chloride for example does not consist of NaCl molecules, as was at one time believed, but of sodium ions Na^+ , and chlorine ions Cl^- . Since substances forming strong electrolytes are completely ionised in the solid state it is reasonable to suppose that they are also completely ionised in solution; this is the basis of the modern theory of strong electrolytes. The measurements of conductivity of osmotic pressure, and of freezing and boiling-points imply, however, that not all the ions are free; this is accounted for by the electrical attraction of an ion for others of opposite sign. The mathematical implications of this point of view were first studied by Professor S. R. Milner, of the University of Sheffield, in 1912, but the work did not receive the attention it merited, partly because of the difficulty of the calculations and partly because the theory was ahead of contemporary developments in other subjects. In 1923 the times were more propitious, and a simpler mathematical treatment was developed by Professor P. Debye with his colleague Dr. E. Hückel, at Zürich. The new ideas have met with remarkable success, and although they are by no means complete and require much modification, they are finding frequent application in the problems of electrochemistry.

When two electrodes, connected to a battery, are placed in a solution of electrolyte the applied electrical force directs the ions, which are present, towards the electrodes; in this way the current is carried through the solution and certain phenomena, such as the liberation of gas or the deposition of a metal, are observed to occur at the electrode. This process of the passage of electricity through a solution is called "electrolysis," a subject first studied in an exact manner by Faraday (see p. 94).

The laws of electrolysis indicate the relation of electrolytic decomposition to the ordinary chemical doctrine of valency, which is the name given to the combining power of an element. A molecule of hydrogen chloride, HCl , is resolved into 1 part by weight of hydrogen and $35\frac{1}{2}$ parts by weight of chlorine. According to the law of electro-chemical equivalents, if the same current

passes through a solution of common salt, NaCl , and then through solutions of calcium chloride, gold chloride, and tin chloride, for every $35\frac{1}{2}$ parts of chlorine set free in the first cell, the same amount of chlorine would be liberated in each of the others. But while $35\frac{1}{2}$ parts of chlorine combine with 23 parts of sodium, which is the atomic weight of that metal, the same quantity combines with 20 parts of calcium, with $65\frac{3}{4}$ parts of gold, and with $29\frac{3}{4}$ parts of tin, and these are respectively $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ the atomic weights of those metals. But since the atomic weights are known from other considerations we must suppose that an atom of calcium combines with twice as much chlorine as an atom of sodium, an atom of gold with three times as much, and an atom of tin with four times as much. And these metals are respectively said to be univalent, bivalent, trivalent, and quadrivalent. Chemically equivalent atoms carry in electrolysis the same electric charge, and the charge carried by one atom of hydrogen or one atom of chlorine is called the unit charge, and is represented by 96,500 coulombs of electricity for 1 gram of hydrogen.¹ The atom of calcium, therefore, carries two such unit charges, an atom of gold three, and an atom of tin four unit charges of electricity.

Industrial processes based on electrolysis are now common. Such are, for example, the modern methods by which such metals as sodium, aluminium, and zinc are obtained, and copper is refined, and electro-plating with silver, gold, nickel, zinc, cadmium, chromium, rhodium, and brass is carried out. In addition to the deposition of metals there is also the liberation of hydrogen, now required on a very large scale, by electrolysis of aqueous solutions. The liquid round the anode in any electrolytic arrangement is exposed to oxidising influence, while the cathode provides a means of reduction, and both these effects are now turned to account for manufacturing a considerable number of salts and other compounds formerly procured by purely chemical processes. Falling water is frequently the source of the energy which is transmuted through the current into chemical energy and heat in the cells, and at Niagara, for example, there has been a large development of electrical industries on both the Canadian and American sides.

Potassium chlorate is an important compound formerly made

¹ No explanation can be given here of the electrical units, definitions of which will be found in every text-book of physics.

by passing chlorine gas into alkaline solutions. It is now made almost exclusively by the electrolysis of potassium chloride solution, keeping the liquid at about $70^{\circ}\text{C}.$, at which temperature the hypochlorite formed at lower temperature is changed into a mixture of chlorate and chloride. When the electrolytic cell is divided by a diaphragm so that the electrodes are kept separate the electrolysis of sodium chloride may be arranged to yield caustic soda and hydrogen gas at the cathode, with chlorine at the anode. The caustic soda is in the solution, and when the decomposition is effected in a suitable cell it is obtained free from common salt. The gases may be led off and utilised in any way desired; the combination of the two gases to produce hydrochloric acid in solution is the modern method for obtaining this important article of commerce (spirits of salts, or muriatic acid).

Another important product is permanganate, which was formerly prepared by fusing together black oxide of manganese and potassium hydroxide or carbonate, whereby a green manganate, K_2MnO_4 , is formed. By passing carbon dioxide through the solution one-third of the manganese was precipitated as dioxide MnO_2 , while the potassium carbonate and permanganate were left in solution. In order to prevent waste of potash the manganate may be dissolved from the fused mass by water, and submitted to electrolysis with iron electrodes at a temperature of about 66° , when the manganate is oxidised to permanganate. Other salts, such as perchlorates, perborates, and persulphates are obtained on a large scale by electrolytic oxidation methods.

On the other hand, the electrolytic method is applied to reduction, and a good example is afforded by the preparation of hydroxylamine from nitric acid. The electrolyte is sulphuric acid of 40 per cent strength, to which nitric acid is slowly added while the whole is kept cool. The hydroxylamine crystallises from the liquid in the form of sulphate and the yield is almost theoretical.

By the use of a cathode cell and appropriate current density, temperature and dilution many organic compounds may be similarly produced with results, as to yield, which in many cases are superior to the older methods of reduction by means of sodium, sodium amalgam, or zinc dust and acid.

CHAPTER XI

THE ARCHITECTURE OF MOLECULES—VALENCY

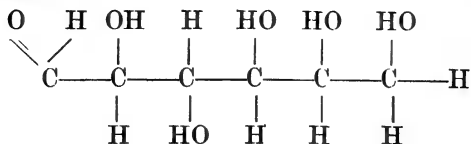
THE term "valency" has been used from time to time throughout the earlier portions of this book, and it has been indicated that it represents the combining power of an element. Stated numerically, it refers in general to the number of atoms of hydrogen or of chlorine, both of which have a valency of unity, or twice the number of oxygen atoms, which has a valency of two, able to combine with an atom of a given element. For example, carbon combines with hydrogen and oxygen to form the compounds CH_4 (methane) and CO_2 (carbon dioxide), and in these its valency is obviously four; in the great majority of its compounds carbon is said to be quadri-valent. Over eighty years ago the germ of the doctrine of valency was recognised by P. F. Frankland, and it has been the subject of constant experiment, enquiry and discussion down to the present day, for the question of what determines the combining power of an element is one of the fundamental problems of chemistry.

It was seen in the last chapter that acids, bases and salts are split up into ions in solution and conduct the electric current; the type of union between the elements in such compounds must be different from those existing in compounds not capable of conducting electricity. Consider, for example, chlorine when in the form of the chloride of hydrogen (hydrochloric acid when in solution) or of a metal, e.g. sodium chloride: the solutions are good electrical conductors, and if silver nitrate is added a white precipitate of silver chloride is obtained. But the compounds



and many others in which the chlorine is directly attached to carbon, show no signs of response to common reagents which react with chlorides of metals. Thus chloroform, CHCl_3 , does not give a white precipitate with silver nitrate, neither does its solution conduct an electric current. An alkali generally contains an HO group and an acid a H atom capable of forming

HO^- and H^+ ions, respectively, but in a sugar, such as the one represented here



there are five hydroxyl groups, HO , and more than an equivalent number of hydrogen atoms, but neither hydroxyl nor hydrogen is capable of separating from the carbon so as to form an ion. It is evident that certain elements or groups, such as chlorine, hydrogen, and hydroxyl, are capable of taking part in two kinds of valency.

Another interesting problem in valency is presented by the complex compounds formed by the union of the salts of certain metals, such as platinum and cobalt, with ammonia. Many of these, and other related compounds have been long known, but their constitution remained a puzzle. In 1892 the late Professor Alfred Werner,¹ of Zürich, reported the results of a careful investigation into the composition and properties of these compounds; he showed that only a portion of the groups of atoms attached to the central nucleus, e.g. platinum or cobalt, is capable of forming ions, and so becoming chemically reactive. Those which are not ionisable, he suggested were connected by a peculiar "subsidiary" valency, called the "co-ordination" valency. Why should some groups be attached by one kind of valency and others by a different kind?

Then there is the problem of the crystallisation of many salts with a definite number of molecules of water. Sodium chloride (common salt) generally has the formula NaCl , but from a cooled saturated solution it is possible to obtain crystals

¹ Alfred Werner was born at Mulhouse, France, on December 12th, 1866; in 1886 he went to Zurich to study, and thence proceeded to Paris. In 1893 he was appointed "extra-ordinary" Professor of Chemistry at Zürich, and made an "ordinary" Professor two years later; this post he held until his death on November 15th, 1919. Werner's main contribution to chemistry was his enunciation of the co-ordination theory of valency, which not only enabled many complex compounds to be classified, but by bringing to light new and unsuspected cases of stereo-isomerism gave a great stimulus to research; for this work he was awarded the Nobel Prize in 1913. Werner's book, *Neuere Anschauungen auf dem Gebiete der Anorganische Chemie*, which has been translated into English, forms an exposition of the importance of his work.

of $\text{Na Cl} \cdot 2\text{H}_2\text{O}$, two molecules of water being attached to each molecule of salt. An immense number of compounds of a similar character are known containing this "water of crystallisation"; for example :

Washing soda	.	.	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Epsom salt	.	.	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Blue vitriol	.	.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Hypo	.	.	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

What is the nature of the bond which holds together the molecule of the salt and the molecules of salt no theory yet explains completely, although it is possible that the hypothesis of Werner may apply in certain cases.

As a result of developments connected with the study of atomic structure we are now able to offer some suggestions which may eventually help to clarify the whole complex problem of valency.

In the description of the nucleus theory of atomic structure (chapter VIII) it was stated that the space of the atom surrounding the nucleus is supposed to be occupied by a number of electrons, equal to the atomic number, but nothing was said about the arrangement of these electrons. When it is remembered that the number increases steadily from hydrogen to uranium, through the periodic table, from 1 to 92, the question of the disposition of these electrons is of importance. From a study of the spectra and chemical properties of the elements, and from various mathematical calculations it has been concluded that the "orbital" electrons arrange themselves around the nucleus in a series of shells or groups, the maximum number of electrons capable of occupying successive shells being

$$2, 8, 18, 32, (50 ?)$$

The significance of these apparently haphazard numbers will be better realised when they are written

$$2 \times 1^2, 2 \times 2^2, 2 \times 3^2, 2 \times 4^2, 2 \times 5^2.$$

In passing from atom to atom in the periodic table these shells become gradually filled with electrons, and as is to be expected the theory attributes similar structures to elements occupying the same vertical groups of the table. Let us consider the inert elements of the zero group, namely helium, neon, argon, krypton, xenon, and radon : these have atomic numbers 2, 10, 18, 36,

54, and 86 respectively, representing their ordinal numbers in the periodic table, and the distribution of the electrons between the various shells is probably represented by the following scheme :

Element.	Atomic number.	Electron Shell.					
		1st.	2nd.	3rd.	4th.	5th.	6th.
Helium	2	2	—	—	—	—	—
Neon	10	2	8	—	—	—	—
Argon	18	2	8	8	—	—	—
Krypton	36	2	8	18	8	—	—
Xenon	54	2	8	18	18	8	—
Radon	86	2	8	18	32	18	8

A consideration of this arrangement shows that, apart from helium, each of these inert elements has eight electrons in its outermost shell: it appears probable that complete chemical satisfaction, leading to an absence of any tendency to react with other substances, is attained by a group of eight electrons. This is one of the fundamental concepts of the modern theory of valency.

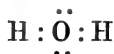
Since the beginning of the present century scientists have speculated concerning the possibility of valency being connected in some way with electrons; in fact in his Presidential address to the Chemical Society on March 26th, 1908 (*Journal*, 1908, p. 774) Ramsay said: "the hypothesis admits of short statement . . . electrons serve as the 'bond of union' between atom and atom," but the time was not then ripe for the development of this idea. The year 1916 marks the commencement of a new era, when the suggestions made by Professor A. Kossel, in Germany, and by Professor G. N. Lewis, in California, followed soon afterwards by the contributions of Dr. Irving Langmuir,¹ laid the foundations of the modern electronic theory of valency.

Previous workers, as for example Ramsay, had attempted to identify the valency bond with a single electron, but Lewis pointed out that of the hundreds of thousands of compounds

¹ Irving Langmuir, born at Brooklyn, New York, on January 31st, 1881, studied at the Columbia School of Mines and at the Göttingen. After teaching chemistry for three years, he was appointed to do physical chemistry research for the General Electric Company of Schenectady, New York, in 1909; he still holds a high research position with this company. Langmuir invented the gas-filled (half-watt) lamp, the condensation pump for obtaining very high vacua, and the atomic hydrogen blow-pipe; he also helped very materially in the clarification of our ideas on the subject of valency.

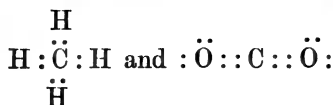
known to the chemist all except a mere handful—not more than five or six—had an *even* number of electrons. This suggested the idea that the valency bond consists in general of a *pair* or “duplet” of electrons, a concept which, when added to that of the stable group of eight electrons, enabled a great step forward to be made. Chemical combination may be regarded as resulting from the tendency to form a complete shell of eight electrons, or “octet,” from the last incomplete shell of the atom, a tendency which can be aided by the sharing of electrons in pairs between different atoms. There is one simple case, which will be readily comprehended, to which the octet rule does not apply, and that is hydrogen; the corresponding stable shell to which it must attain is that of helium, namely, one containing two electrons only.

Let us now consider the application of these views to a simple case, such as the combination of hydrogen and oxygen; the former has one electron, but would be stable with two, and the latter has six electrons in its outer shell,¹ but would like to have eight. Now both of these elements can have their requirements satisfied if the two hydrogen atoms each contribute an electron towards a pair shared with an oxygen atom forming water; which may be represented as



It will be noted that a shared pair of electrons counts towards satisfying the needs of both the atoms which it unites. Since each duplet of electrons shared represents a valency it will be seen that hydrogen has a valency of one, whereas oxygen has a valency of two; this is in harmony with the generally accepted ideas and of the accepted formula H_2O for water.

An atom of carbon has four electrons in its outer shell, consequently it is able to share four more with other atoms, as, for example, in methane (CH_4) and carbon dioxide (CO_2), thus



¹ It should be noted that the atomic number of oxygen is eight, and so there are eight orbital electrons; of these two are in the first shell and do not count towards valency, and it is only the six in the outer incomplete group which must be considered.

In the latter it will be observed that the carbon atom shares *four* electrons with each oxygen atom: each valency is then known as a "double bond"; in both compounds it is evident that the carbon atom is sharing a total of four duplets with other atoms, and so it has a valency of four, as has long been known.

The valency shell of the nitrogen atom has five electrons, and so it is able to combine with three atoms of hydrogen giving the compound NH_3 , ammonia, the nitrogen having a valency of three.

It is unnecessary to multiply examples further, except to mention the case of the element chlorine: this has seven electrons in the outermost shell, and is consequently able to complete its octet by sharing with one other atom, e.g., with an atom of hydrogen to form hydrogen chloride, HCl , or another atom of chlorine to give a molecule of chlorine, Cl_2 , thus:



Attention must be called to the fact that all the compounds mentioned, with the exception of hydrogen chloride in aqueous solution, and in fact all those in which the atoms are joined by electron pairs are non-electrolytes and do not conduct the electric current; this type of valency has been called "covalency." Even hydrogen chloride is a non-conductor in the pure state and only conducts electricity if dissolved in water, when its structure changes.

It now remains to be seen how the electronic theory accounts for electrolytic compounds: consider the case of the salt sodium chloride, made up of sodium and chlorine; the atomic numbers of these two elements are 11 and 9, respectively, and the arrangements of the electrons in their shells may be written 2, 8, 1, and 2, 7. The sodium atom has, therefore, one electron in its outermost shell whereas chlorine has seven, and the question arises: how can these two elements combine and simultaneously satisfy the octet rule? The answer is, by the one electron from sodium passing completely over to the chlorine, making both atoms have the arrangement 2, 8, although no sharing occurs. But it will be noted that the sodium has one electron less than the charge on its nucleus¹ (11) and so as a whole it has a net unit

¹ This is, of course, equal to the atomic number (see p. 120).

positive charge, and it is in fact the ion Na^+ ; similarly, chlorine has one electron in excess of the nuclear charge, and so it is a negative ion, Cl^- . If these two oppositely charged ions are now held together by forces of electrical attraction, we have a picture of sodium chloride which is in excellent harmony with its known properties, particularly the ability to give an ionised solution capable of conducting the electric current.

The element calcium has two electrons in its outermost shell and it therefore forms an ion with two positive charges, Ca^{++} , by giving these up to other atoms, for example to two atoms of chlorine; the formula of calcium chloride, CaCl_2 , would thus be written $\text{Cl}^- \text{Ca}^{++} \text{Cl}^-$, each atom having a complete octet of electrons, but none being shared. The type of valency here described, resulting from the complete transfer of an electron from one atom, generally of a metal, to another, generally a non-metal or non-metallic group, is called "electrovalency," and it is always associated with electrical conductivity. It is interesting to note how close to the concept of electrovalency were the ideas expressed by Ramsay in his Address of 1908, already mentioned.

Some evidence that in a crystal of a salt, such as sodium chloride, the unit of structure is not the molecule of sodium chloride but the separate ions, is obtained from the work of Sir William Bragg and of his son Professor W. L. Bragg on the "diffraction" of X-rays by crystals. It appears that the crystal of sodium chloride is built up of separate sodium units and chlorine units, and not of sodium chloride units, as in the case, for example, of stannic chloride, in which the chlorine atoms are joined to the tin atom by covalency links. There is no definite proof that the sodium and chlorine units are ions, but it appears to be highly probable that this is the case. As already seen, in the previous chapter, the idea of the existence of ions in the crystals of strong electrolytes leads to the new concept of complete ionisation in solution, which has proved such a valuable guide to the modern treatment of such electrolytes.

In conclusion brief mention may be made of the application of the electronic theory to Werner's ideas, already described, concerning the nature of complex molecules. The ionisable portions of the molecule are obviously attached by electrovalencies, but the so-called subsidiary, or co-ordination, valency

is now identified with a special type of covalent bond in which *both* electrons forming the pair come from one of the combining units. The name co-ordinate link or bond is generally given to this type of valency which has been found to occur in numerous compounds, and may to some extent account for the formulation of salts with molecules of "water of crystallisation" to which reference has already been made.

STEREO-CHEMISTRY

It cannot be claimed that all the problems of chemical linkage or valency have yet been cleared up, but the development of the electronic theory has marked one of the most significant advances in theoretical chemistry during the present century. It has been, of course, impossible to give more than an outline of it here, but it is hoped that sufficient has been said to indicate the lines along which it has progressed: those who have sufficient knowledge and interest in the subject to wish to know more of the subject must refer to the modern treatises.

A natural sequel to a discussion of the combining power of the elements is to consider how the valency bonds are arranged in space: clearly in salts, and similar compounds, in which the component parts are held together by electrical forces only, the question of direction cannot arise, but when elements are joined by the definite sharing of a pair of electrons, as in covalent bonds of various types, there must be some definite spatial arrangement in the molecule.

We may begin by recalling the fact that Dalton and several of the early promoters of his atomic theory were led to consider, though without giving the subject much attention, the question of the arrangement which chemically combined atoms assume in space of three dimensions. If a detached molecule could be seen, what would it look like? There is a great deal of evidence, some of which is indicated in a preceding chapter, that each atom retains its independence, so that there is a certain rough analogy between the bricks in a wall and the atoms in a molecule. Dalton, referring to the diagrammatic representations of atoms in his *Chemical Philosophy*, Part I (1808), says:

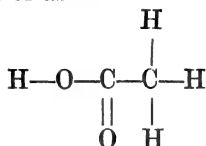
"The combinations consist in the juxtaposition of two or more of these (atoms); when three or more particles of elastic fluids are combined together in one it is to be supposed that the

particles of the same kind repel each other and therefore take their stations accordingly."

Dalton also gives diagrams showing the arrangements which he supposed might exist in a number of different compounds, including a substance so complex as alum.

Wollaston about the same time recognised that it would be necessary "to acquire a geometrical conception of their relative arrangements in all the three dimensions of solid extension."

"Constitutional" formulæ based on notions of valency began to be used soon after 1860, but these formulæ had no pretension to representing the relative positions of atoms in space. They served merely to show in what order the atoms were supposed to be linked one to another in a molecule, and thus served to some extent to epitomise the chief chemical changes to which the compound would be liable. Thus if acetic acid was represented as $\text{CH}_3\text{CO.OH}$ or as



the latter was not designed to serve as a picture of a molecule, though such formulæ have been and are very valuable for distinguishing the more prominent cases of *isomerism*, that is of compounds which, while possessing the same composition, have different chemical properties, and hence, presumably, different atomic structure.

An acid called lactic acid is produced in sour milk, and another acid having the same composition occurs in flesh, and hence is found in Liebig's meat extract. These acids have the formula $\text{CH}_3\text{CHOH.COOH}$. They are very much alike, but the latter of these acids is optically active—that is it causes the rotation of a plane polarised ray¹—while the other is inactive. The study of these acids by Wislicenus in 1872-3 led to the idea that the differences observed could only be accounted for by supposing different relative positions to be assumed by their constituent atoms in space of three dimensions. But it was not till 1875 that a complete theory was conceived by the late Dutch professor Van 't Hoff, and set forth in his treatise *La Chimie*

¹ See *Polarimeter*, p. 81.

dans l'Espace. Almost simultaneously the connection between optical activity and asymmetry was discovered by the French chemist J. A. Le Bel, and so began the study of *Stereo-chemistry*, that is of the arrangement in space of the constituent parts of a molecule.

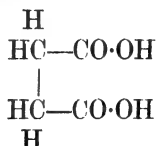
The theory is based on the following recognised facts :

1. The four units of valency of carbon are equal in every respect. In the mono-substitution derivatives of marsh-gas CH_4 and ethane C_2H_6 no isomeric modifications have been discovered.

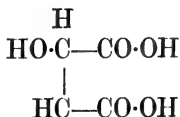
2. All compounds of carbon which in the liquid state rotate a polarised ray, or when crystallised produce hemihedral forms which are mirror-images of each other, are found to contain at least one atom of carbon which is united directly to four dissimilar atoms or groups of atoms, and which is therefore said to be asymmetric.

3. Compounds which are known to contain asymmetric carbon, and which, nevertheless, do not exhibit optical activity, are generally resolvable by one or other of several known processes into two compounds, each of which possesses rotatory power equal and opposite in direction to the rotatory power of the other.

Succinic acid, for example,



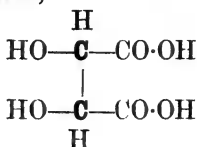
is optically inactive ; but when one of the hydrogen atoms is replaced by hydroxyl, so that the C to which it is attached becomes "asymmetric," the result is the production of malic acid,



which exists in two isomeric forms, one of which rotates the polarised ray to the right, the other to the left.

An apparent exception is represented by mesotartaric acid, which has the same composition as (1) ordinary, dextro-, tartaric acid, (2) racemic acid which is found in the grapes of certain districts, and (3) lævo-tartaric acid which is obtainable along with

the dextro-acid from racemic acid. Mesotartaric acid is not resolvable into two acids, like racemic acid, and therefore cannot be regarded as composed of the other two. But it contains within the molecule two asymmetric carbon atoms indicated by heavy type in the formula,



and the action of one of these on the polarised ray may be supposed to be equal and opposite to the action of the other, so that the effect is the same as if they existed in separate molecules, mixed together in exactly equal numbers, as in the case of racemic acid.

Van 't Hoff's hypothesis, which serves to explain these facts, supposes the carbon atom to be situated at the centre of a regular tetrahedron, while the four other atoms united with it are situated at the solid angles ; so that the four valencies of the carbon atom are supposed to operate in the directions of four radii of a sphere included in the tetrahedron or which includes it.

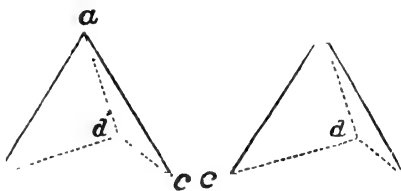
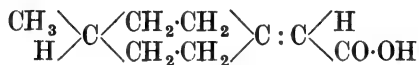


FIG. 52.

Suppose the atoms united with a carbon atom to be represented by letters, then when one atom of carbon is united with $4a$, with $3a+1b$, with $2a+2b$ or with $2a+1b+1c$ isomerism is impossible, that is, there can exist only one compound of this constitution. But when all four of the attached atoms or groups of atoms, a , b , c , d , are different two cases occur. These are represented in Fig. 52 ; it will be observed that one of these is obviously a reflection of the other, and is not superposable upon it in such a way that the letters coincide. The use of models assists materially in the consideration of stereo-chemical problems.

Within the last few years many cases have become known in which apparently the existence of an asymmetric atom of carbon within the molecule is not essential to the development of optical activity. It appears, therefore, that a modification of the original theory is necessary so as to include those compounds which are optically active, and whose activity can only be attributed to a want of symmetry in *the molecule considered as a whole*.

The first compounds of this type were obtained in 1909 by Professors Perkin, Pope, and Wallach, and one of them is represented by the formula below :



Here there is no carbon atom which is asymmetric according to Van 't Hoff's definition ; nevertheless it is obtainable in a right-handed and left-handed form, which may be accounted for by supposing the two groups at one extremity to lie in the plane of the paper, while the other two stand the one above and the other below the paper.

The presence of a double bond C : C in a molecule, as in the one just depicted, raises an interesting point : how may we

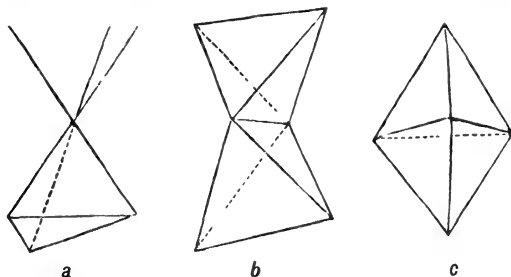
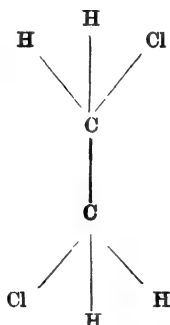


FIG. 53.

picture such a bond on the basis of the tetrahedral representation of carbon atoms ? If two carbon atoms are joined by a single linkage, C—C, then the union may be pictured as in Fig. 53 (a), that is with a point of one tetrahedron joined to that of another ; on this basis a double bond, C=C, involves two

tetrahedra being connected by two points, that is along an edge as in Fig. 53 (b). A triple bond, $C\equiv C$, incidentally may be represented as at (c). It will be seen from these diagrams, as Van 't Hoff pointed out long ago, that when two carbon atoms are united together by a single bond they are evidently able to rotate freely about an axis which is the line representing the direction of the uniting valencies, but if two carbons are joined by two or more bonds rotation becomes impossible. This fact has important consequences.

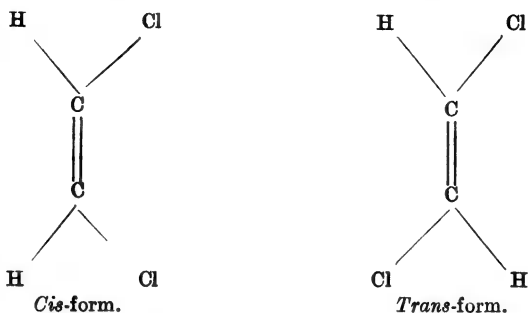
Consider the compound ethylene dichloride, $C_2H_4Cl_2$, which may be represented diagrammatically, thus :



It might be imagined at first sight that several different forms of this substance are possible, according to the relative positions occupied by the two carbon atoms about the bond uniting them ; if the atoms can rotate freely about this bond as an axis, then theoretically every possible position can occur, and the actual substance as isolated should consist of an infinite number of forms continually changing into one another by rotation, so that no one can be identified from any other. Only one kind of ethylene dichloride is known, therefore, in which every possible relative position of the carbon atoms occurs, although recent work has indicated that certain positions, such as the one shown above in which the chlorine atoms are kept far apart, are preferred to some extent over the others. This is probably a result of the repulsion of the similar atoms, aided perhaps by the attraction of the hydrogen and chlorine atoms.

If the molecule contains a double bond, as in dichloroethylene $C_2H_2Cl_2$, for example, the position is quite changed ; it can be

easily seen that two different configurations of the carbon atoms are possible, thus :



in which the similar atoms are either on the same side, called the *cis*-form, or on opposite sides, as in the *trans*-form. Since rotation about the C=C bond is not possible it is evident that these two structures must represent two different substances, although they have the same ultimate formula. The two forms of dichloroethylene have been isolated and are well known, and their properties are such as might be expected from their respective structures. Although these two substances are stereoisomers it must be emphasised that they do not display optical activity; this is only to be expected from the fact that the two forms are not mirror images of one another. Many examples of this type of isomerism are known, and it is generally called "geometrical isomerism" to distinguish it from the type in which the isomers are optically active.

It may now be interesting to the general reader to learn what progress has been made in the application of space chemistry to elements other than carbon, which so far has alone been referred to.

Nitrogen presents itself first, and a case of nitrogen asymmetry, corresponding to carbon asymmetry, has been observed by Le Bel in the compound methyl-ethyl-propyl-isobutyl ammonium chloride :



Here the four radicals are attached in the same kind of way to the nitrogen¹, and in accordance with the principles already

¹ It should be noted that the fifth radical, which is chlorine, is held to the rest of the molecule by an electrovalency, and so occupies no definite position in space.

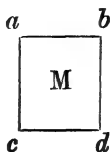
explained there may be two arrangements, one of which is the mirror image of the other.

A few years later, in 1899, a compound of similar constitution was obtained by Professor Pope and Mr. Peachey and resolved into optically active dextro- and lævo- compounds.

Since the time referred to discoveries have followed one another in rapid succession. Pope and Peachey, and at nearly the same time S. Smiles, succeeded in isolating optically active compounds, of which the atom of sulphur was the directing nucleus. These were followed by compounds of tin, silicon, phosphorus, arsenic, selenium and boron, which have been shown to be endowed with the same property. And there appears to be no doubt that most of the elements to be found in Groups IV and VI of the periodic scheme may gather round them groups of other atoms in tridimensional space and can thus act as centres of optical activity.

Perhaps still more remarkable was the announcement in 1911 from the laboratory of Professor Werner of Zürich, whose views were briefly referred to earlier in this chapter. From an examination of the complex ammonia compounds, called ammines, produced by several metals, especially platinum, chromium and cobalt, he has been able to prove that metals can act as the central nuclei of stable asymmetric molecules, which may be resolved into optical isomerides exhibiting the optical activity corresponding to that of carbon compounds. A number of metals have also been shown to act as centres for geometrical isomerism not involving optical activity.

In this connection it is interesting to note that certain metals, for example, platinum, palladium, and nickel, when exerting a valency of four do not have the tetrahedral arrangement in space associated with carbon, nitrogen, etc. This is not surprising since the metals mentioned have quite different electronic structures, and are capable of exerting a variety of valency states. It appears that in many compounds of the metals mentioned the four valencies are to be regarded as being in one plane, directed towards the four corners of a square. A molecule of the type $M a b c d$ would thus be represented :



and it requires little consideration to realise that such a compound does *not* exist in two isomeric forms ; but when substances of a simpler type, Ma_2b_2 for example, are examined it is found that geometrical isomerism is possible, without optical activity. The two forms, which may be compared with the *cis*- and *trans*-forms of dichloroethylene, can be represented thus :



and such isomers have been definitely isolated and studied.

Numerous examples of stereo-isomerism of different types are known, but at this point the difficulties of the problems involved multiply to such an extent that without a considerable acquaintance with the compounds it would be impossible to communicate further information on this most interesting department of chemistry. Moreover for complete demonstration models are necessary. For the student, therefore, who desires to pursue the study of stereo-chemical theory the larger treatises and the current periodical literature must be consulted.

CHAPTER XII

CATALYSIS AND CATALYSTS

THESE look like very hard words, but as *catalyst* is derived from the Greek, which merely means an agent which *unloosens* or sets free something else, they can be regarded as reasonable in their application, and not, as appears in some other cases, a device for concealing ignorance.

An example will make the matter clear. Oxygen mixed with twice its volume of hydrogen forms a mixture which is well known to explode on approach of a flame or an electric spark, or when heated strongly enough in any other way. This mixture of gases may be kept indefinitely in a closed vessel in the dark or in sunlight without the production of water or any other sign

of chemical combination. If, however, a perfectly clean piece of platinum foil is introduced into the mixture combination between the oxygen and hydrogen immediately begins, and often proceeds so rapidly that the metal becomes red hot and ultimately the residual gas explodes. But when the action is all over the platinum betrays no sign of having had anything to do with the matter. It is unaltered in weight and appearance and, if unsoiled by handling or otherwise, it retains the peculiar catalytic property which it has just manifested.

The facts just related were discovered so long ago as 1817 by Sir Humphry Davy, who, with the aid of a spiral of platinum wire suspended in a glass containing a little alcohol or ether, demonstrated the union of the vapours with the oxygen of the air on the surface of the metal, producing what he called his "lamp without flame." Many observations of the same kind made by later experimenters proved that the effect was producible by many substances beside platinum.

Catalysis, then, is a process in which a chemical change, which without assistance proceeds either not at all or very slowly, is greatly accelerated by contact of the materials with a small quantity of some agent, called the catalyst, which remains after the reaction undiminished.

The catalyst in some cases retains in its appearance some evidence of having suffered change, but chemically it remains quite unaltered. It is, however, possible frequently to account for the starting and continuance of the observed chemical action by the hypothesis of the alternate formation and decomposition of a compound of the catalyst with some constituent of the materials engaged in the change. Thus in the process frequently employed for procuring oxygen by heating potassium chlorate with a relatively small quantity of manganese dioxide, it is probable that the action consisted essentially in the formation of an oxide of manganese containing a larger proportion of oxygen than the dioxide employed, and its subsequent decomposition so that the dioxide remained at the end.

In this case evidence is derived from the altered appearance of the oxide left behind, and also from the two facts that the oxygen thus obtained always contains a trace of chlorine, while the residual potassium chloride is alkaline from the formation of a trace of potassium oxide.

On enquiry among the numerous and various instances of

catalytic action, among carbon compounds especially, it appears that no explanation can be found which is applicable generally. All that can be said is that the action is in many cases chemical and that it involves the alternate formation and destruction of an unstable compound. In many instances, however, there is no evidence for the definite formation of an unstable intermediate, and for these cases of catalysis an alternative mechanism is proposed. If the catalyst is a solid and the reacting substances gases, then it is suggested that the molecules of one of the latter attach themselves to the surface of the solid catalyst, possibly by electrical forces involving the movement of electrons. This results in a loosening¹ of the valency linkages in the attached gas molecule, so that when another molecule approaches it the two molecules are much more ready to combine than they would be normally.

Although examples of solid catalysts are probably most common, there are numerous examples in which catalytic action occurs in a system consisting of liquids or of gases only, or of a liquid and a gas. There is the case, for instance, of the action of almost any acid on a solution of cane sugar as a result of which it is converted into "invert" sugar, a mixture of equal quantities of glucose and fructose, or the action of a few drops of sulphuric acid on aldehyde whereby in a few minutes it is converted, with evolution of heat, into paraldehyde, a compound having the same composition as aldehyde but three times the molecular weight. The preservative effect may also be cited of a minute quantity of sulphuric or phosphoric acid on hydrocyanic (prussic) acid, which in its absence passes quickly into a mixture of ammonium formate and a brown substance.

One very interesting case in which a minute quantity of a third substance affects the mutual behaviour of two others is provided in those numerous instances in which the presence of traces of water vapour seem to be essential to interaction. It certainly appears to be so when chlorine is brought into contact with metals, for even metallic sodium may be preserved for years in contact with chlorine gas at common temperatures if the latter is perfectly dry, and the indifference of combustible substances such as carbon monoxide gas, charcoal, and

¹ It is remarkable that the modern view of many catalytic actions appears to coincide with what Berzelius had in mind when he coined the word "catalysis" in 1835.

phosphorus to oxygen gas when all are free from moisture has been the subject of much experimental enquiry.

The catalytic combination of acetylene with water to form acetaldehyde, which is the material from which large quantities of acetic acid are now prepared, is of interest, because the catalyst is mercuric sulphate dissolved in the water. Here we have an illustration of catalysis involving gas and liquid only.

Catalytic agents are employed in many industrial operations. An example of catalytic effect is to be found in the long-established lead-chamber process for making sulphuric acid, in which sulphur dioxide, water, and atmospheric oxygen are enabled to interact rapidly in the presence of a relatively small proportion of nitrogen dioxide NO_2 . Here several intermediate nitrogenous compounds are undoubtedly formed, but whether they are essential stages in the process by which sulphuric acid is ultimately produced from its dissociated constituents is a question which cannot be regarded as even yet finally settled. The lead chamber survives, but of late years has found a serious rival in the "Contact" process, which is merely the outcome of a long known catalytic operation based on the use of finely divided platinum. Theoretically sulphur dioxide requires one atom of oxygen to convert it into sulphur trioxide, $\text{SO}_2 + \text{O} = \text{SO}_3$. The process is, however, a relatively slow one, and so it is necessary to use a catalyst in order to make it take place more rapidly. This combination is attended by the evolution of a considerable amount of heat, which, if allowed to accumulate, so as to raise too high the temperature of the tubes containing the contact substance, will partly undo the result of the combination, and the sulphur trioxide is destroyed. Another point to attend to is the necessity for providing a considerable excess of oxygen in the form of atmospheric air, the nitrogen of which takes no part in the change. The platinum is used in the form of a deposit of fine particles on asbestos fibre, which is easily produced by soaking the asbestos in a solution of platinic chloride, drying it and then exposing to a low red heat by which the chloride is completely decomposed. Since platinum has become so costly as it now is, many attempts have been made to replace it by other substances, and many patents have been taken out. Ferric oxide (red oxide of iron) has been used, but it is definitely less effective than platinum. Recently vanadium pentoxide has been employed for catalysing the combination of sulphur

dioxide and oxygen, and it bids fair to become a serious rival to platinum.

In connection with the use of platinum a discovery was made in the earliest days of this process which for a time checked its development and even threatened failure. The fact came out that minute quantities of certain substances have the property of "poisoning" the catalyst, so that its activity pretty rapidly declines, and it becomes "dead." Fortunately this was traced to the impurities which accompany the sulphur dioxide produced by roasting iron pyrites. Of these the most important is arsenic. By cooling and spraying with water the gases brought from the pyrites ovens these impurities can be removed and the gas, cleared of mist, can be safely delivered into the series of pipes charged with the platinised asbestos. An alternative method which is coming into general use is to precipitate the dust by making the gas pass between plates electrically charged to a high voltage; this is called "electrical precipitation," and is really an application of the colloidal properties discussed in the next chapter.

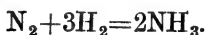
The Claus kiln affords another example of a catalytic process which has been turned to account for industrial purposes. In the production of soda, that is sodium carbonate, from common salt by the Leblanc process¹ which has been in operation for more than a century, the accumulation of impure calcium sulphide in the form of alkali-maker's waste was for generations a source of loss to the manufacturer, and of annoyance to the district.

Attempts to deal with it proved unsuccessful till about the year 1887 when Messrs. Chance, of Oldbury, succeeded in overcoming the difficulties which had previously stood in the way of success. Their process consisted essentially in decomposing the wet tank waste or impure calcium sulphide with carbon dioxide, obtained from limekiln gases, in such a way as to obtain a gas very rich in sulphuretted hydrogen, the residue being almost inodorous and harmless. The problem then was to get the sulphur out of this gas in a convenient form, so as at once to get rid of the offensive smell and obtain a marketable product. This was done by the use of the catalytic action of ferric oxide, which in the presence of a mixture of sulphuretted hydrogen and a limited quantity of air, slightly warmed, causes the hydrogen to unite with the oxygen while sulphur is set free.

¹ This process is now obsolescent.

The action of the oxide of iron seems to consist in local reduction to a lower oxide and reoxidation by the passing air. A somewhat similar action occurs in the oxide of iron purifier employed in the gas works for the removal of the last portions of sulphuretted hydrogen from coal-gas.

The combination of nitrogen with hydrogen so as to produce ammonia has long been a desideratum. The passage of electric sparks through such a mixture gives rise to the formation of a minute amount of the compound, but inasmuch as ammonia is decomposed by heat the process soon reaches a stage at which equilibrium is established, the ammonia being destroyed as fast as it is formed. Pressure has been found to promote the combination of the two elementary gases in accordance with the rule that pressure in a mixture of gases tends to facilitate the formation of that substance which occupies the smallest volume, in this case the ammonia, as shown by the equation,



The introduction of a catalyst in the form of an active metal greatly increases the yield of ammonia. The manufacture of ammonia by the combination of nitrogen and hydrogen, by what is known as the Haber process, has become of great importance, and so a further discussion and description will be left for the present.

A very pretty and interesting experiment sometimes exhibited in the lecture room consists in bubbling oxygen through a little moderately strong solution of ammonia contained in a flask, in which is suspended a coil of clean platinum wire. White fumes of ammonium nitrate and nitrite appear in the neighbourhood of the coil, and if the supply of oxygen is rapid the flask will become filled with orange-coloured nitrogen dioxide, and the bubbles of gas, containing as they do an explosive mixture of oxygen and ammonia, often burn as they escape from the surface of the liquid and are ignited by the now red-hot metal. In this experiment air may be substituted for oxygen with similar though more moderate effects.

It is perhaps remarkable that these phenomena should have remained unnoticed by the industrial chemist till quite recent times. Early in the present century, however, the conditions of the reaction between ammonia and air in the presence of platinum were investigated by Professor W. Ostwald of Leipzig,

and it was found that the yield of nitric acid amounted to something like 85 per cent of the theoretical. The ammonia mixed with a relatively large volume of air is passed through a number of flat sheets of platinum gauze, or other less expensive catalysts such as one of several metallic oxides, and maintained at a temperature of 300°C . or somewhat higher. This process was used on a large scale in Germany during the war in order to obtain nitric acid for the manufacture of explosives. It is still operated to some extent in many countries, especially to supply the oxides of nitrogen required for the lead-chamber method for making sulphuric acid and for making nitric acid from synthetic ammonia obtained by the Haber process (chapter XXVII).

The researches of Professor Sabatier of Toulouse on combinations of hydrogen effected by the agency of a catalyst date from the extreme end of the last century, and have excited not only great interest among those occupied in scientific chemistry, but have led to unexpected applications to industrial purposes which already have assumed a position of great practical importance.

These researches seem to have originated in attempts, known to have been made by Moissan, to contrive the direct union of acetylene with certain metals such as copper, nickel, and iron. The expected fixation did not take place, but Sabatier found that ethylene, as well as acetylene, when directed on finely divided metals at a temperature of only 300°C . produces incandescence with a deposit of carbon, the escaping gas consisting of hydrogen mixed with ethane. This seemed to indicate that hydrogen had been added to the elements of the ethylene, and by further experiments it was found that a mixture of ethylene and hydrogen passing through a column of reduced nickel is changed into ethane by combination of the two gases: $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$.

In association with M. Senderens further research enabled the enquirers to generalise this result. Even at common temperatures acetylene mixed with excess of hydrogen, in contact with the metal, is completely converted into ethane, without formation of secondary products.

These experiments carried out in 1899 showed that nickel freshly reduced from its oxide possesses this catalytic power in relation to hydrogen in a peculiar degree. Reduced cobalt, iron,

and copper, as well as spongy platinum partake of this property more or less.

Various modifications of the process have since been devised, especially with the object of operating on materials in the state of liquid, without resorting to the process of converting into vapour or gas. At the temperatures necessary for this purpose many carbon compounds are destroyed or seriously altered in composition. These modifications are in many cases successful, but the interaction takes place much more slowly.

As to the chemical changes which are brought about by the process of hydrogenation they may be ranged into several classes. When oxygen is present water is formed in some cases, while in others hydrogen is simply added on. In other cases the molecule is broken up as when benzene, C_6H_6 , is converted by addition of hydrogen into methane or marsh-gas, CH_4 . Aniline is also converted by similar action into hydrocarbons and ammonia which is, of course, produced from the nitrogen detached.

Professor Sabatier explains the action of these metals by the hypothesis of the formation of an unstable temporary hydride of the metal formed by combination of hydrogen with the superficial layers. Such hydride would be easily dissociable, and the hydrogen, therefore, is easily removed by contact with unsaturated compounds.

We may now turn to the consideration of the important practical applications which have arisen out of these apparently recondite investigations. In the first place it is perhaps not inappropriate to observe that they supply a satisfactory answer to those persons who are often disposed to enquire as to the utility of this or that piece of pure scientific work which seeks to extend knowledge without reference to the further use of it. Scientific literature abounds with examples, but this deserves remark, because it is so recent as to be still in process of development. But there is another reason for noticing the present case attentively, and that is that it serves as an example of the common failure of the discoverer to participate in the commercial profit which is made of his discovery. Professor Sabatier has shown the chemist and manufacturer how the element hydrogen may be made to unite with a great diversity of substances, by a process which is easily carried out and which involves the use of no costly materials.

A large proportion of vegetable oils and some animal fats are liquid at the common temperature of the air. They are, therefore, of smaller value for many purposes than the fats which are solid under the same conditions. Consequently many attempts have already been made to act on the oils in such a way as to convert them more or less completely into solid substances. It should be explained that most of the oils consist essentially of a compound called *olein*, which is the ester or compound ether of glycerine with oleic acid. The solid fats are similar compounds derived from stearic or palmitic acid. Stearic acid is so named from the Greek word *στέαρ*, tallow. Palmitic acid occurs abundantly in palm oil. Now these latter acids are what the chemist calls saturated compounds, that is, they contain the carbon, hydrogen, and oxygen, of which they are composed, in such a condition that they fully satisfy their mutual attractions and cannot enter directly into any further chemical union. But olein is unsaturated and can unite with two atoms of hydrogen, forming the corresponding compound of stearic acid.

The most practical of the older attempts to produce a solid fat from oil was based on the fact, discovered long ago, that in contact with nitrous acid olein and oleic acid are converted into solid compounds, called respectively elaidin and elaidic acid. Another method depends on the action of strong sulphuric acid on oleic acid, whereby it is converted into a mixture of solid compounds which require subsequent distillation under reduced pressure.

No sooner had Sabatier made known the nature of his method than numerous patents were taken out by other people with the object of applying his principle to the hydrogenation of unsaturated fats.

The practical feature of these patents consists in the fact that it is only necessary to add the catalyst, usually porous metallic nickel, to the oil, to heat it to a moderate temperature, namely, from 200° to 250° C., and to inject hydrogen gas into the mixture. The result is that the unsaturated oils present combine more or less completely with hydrogen to form the corresponding saturated fat, and thus at the end of the process a product is obtained which has a melting-point considerably above the melting-point of the material operated on. In fact an oily substance is thus hardened into a fat which is solid at common temperatures. The resulting hardened fats are of great commercial

importance, being largely employed especially in soap and candle making. The following extract from a trade report for the year 1913¹ indicates the manufacturer's view of the position :

"In the year 1913 the imports of the hitherto customary raw materials for soap-making, such as tallow, palm oil, and coconut oil, showed a drop of more than 6000 tons. But it must not be concluded from this that the production of British soaps decreased in that year, because the new hardening process has also given to certain other fatty substances, such as whale oil and linseed, which formerly were scarcely of any account, a great importance for the soap industry."

Since this report was written there has been a steady increase in the amount of hardened oils used in the soap industry ; in the year 1933 a total amount of 27,000 tons, consisting mainly of whale, cotton seed, and soya bean oils, were hydrogenated for soap making.

The production of the enormous quantities of hydrogen required in these operations is a question of great practical importance which will be dealt with in a later chapter. It is only necessary to say here that the hydrogen employed must be approximately pure, as the presence of small quantities of sulphur or arsenic compounds serve to diminish the activity of the catalyst, and ultimately to destroy it, as in other cases already referred to. Though the weight of hydrogen actually absorbed by the oil is relatively small, the volume of gas, by reason of its lightness, assumes enormous proportions. One ton of oleic acid requires roughly 79,000 litres or 2800 cubic feet, and one ton of ordinary olein requires 75,900 litres or 2680 cubic feet of hydrogen gas.

A large number of processes have been patented for the preparation of the nickel used as catalyst in an active form. One interesting method proposed was to pass the vapour of the compound of nickel with carbon monoxide, known as nickel carbonyl, together with hydrogen into the oil to be hydrogenated at a temperature of 200° to 240° C. The carbonyl is decomposed at this temperature, forming nickel in a finely divided and active state ; at the moment of formation it was said to be specially effective in permitting the reaction between hydrogen and the oil. The modern methods of preparing the catalyst depend on the reduction of an oxide of nickel. In one of these nickel in the

¹ Meesse. Bigland Sons and Jeffreys, of Liverpool.

form of wire or turnings is enclosed in a gauze cage, and oxidised superficially by use as anode in an electrolytic cell containing an alkaline solution. The oxide is then reduced with hydrogen at 250° ; the temperature is then lowered to 180° C. for the hydrogenation of liquid fats. In another process, a porous mass, such as asbestos or kieselguhr, is impregnated with nickel sulphate, which is then converted to hydroxide by the action of sodium hydroxide (caustic soda). The resulting mass is washed well with water, dried and heated in a current of hydrogen, when finely divided nickel spread over and through the porous material results.

The application of the process is not confined to soap and candle making. Already various inferior oils are being converted into solid fats which, after due purification, are transformed into edible products, which form an appreciable part of margarine, and especially of fats for baking purposes, sold in Great Britain and the United States. It is claimed that the hardened fats are digestible and are absorbed to the extent of 97 per cent; the amount of the nickel remaining in them is so small as to have no harmful effects on human beings.

In this great development the discoverer of the principle and its application has, it is understood, no share. It is gratifying, therefore, to record the award of a Nobel Prize for chemistry to Professor Sabatier.

The process of hydrogenation has been supplemented in an interesting way by the discovery that the same catalytic agents are capable in certain cases of inverting the process, and so causing a disruption of the substance into hydrogen and a residual compound. The alcohols, for example, may be resolved in the presence of copper into hydrogen and aldehyde. The process may be turned to industrial use for the production of formaldehyde from methyl alcohol.

Other catalytic agents have been found among the metallic oxides by the Russian chemists Gregorieff and Ipatieff. Alumina, for instance, at a temperature near 300° , causes generally the dissociation of the primary alcohols into water and the corresponding ethylenic hydrocarbon.

The process of dehydration seems to be always accompanied by dehydrogenation with the production of an aldehyde and hydrogen gas. But whether the one or the other of these changes predominates depends on the nature of the oxide. Thus

thoria, alumina, and tungstic pentoxide are very active in decomposing the vapour of ethyl alcohol at 340° to 350° C., and the gas evolved consists almost entirely of ethylene. Oxides of zinc, manganese, and vanadium, on the other hand, are much less active, and the gas produced is chiefly hydrogen. Alumina at the lower temperature of 240° to 260° splits ethyl alcohol almost entirely into ether and water.

Among processes long recognised as catalytic is the Deacon process for obtaining chlorine. This depends on the interaction of hydrogen chloride gas with the oxygen of air in the presence of cupric chloride. A temperature somewhat over 400° C. is required. The process was introduced more than sixty years ago, but it is now obsolete, since more effective methods for the manufacture of chlorine have been developed.

Two other examples of catalysis which are especially of industrial interest may be mentioned. In the earliest process for the synthetic production of indigo (p. 324) the compound phthalic anhydride was required as an intermediate, and the first stage in its preparation involved heating naphthalene with concentrated sulphuric acid; as a result of an accident it was found that mercury was an excellent catalyst for the process, and this discovery proved to be the turning point in what had previously been an unsuccessful venture. At the present day the naphthalene is oxidised as vapour with the aid of vanadium pentoxide as catalyst.

A very new application of catalysis is to be found in the manufacture of synthetic methyl alcohol, now used on a large scale for the preparation of formaldehyde for synthetic resins (chapter XXV). A mixture of carbon monoxide and hydrogen (water gas), or of carbon dioxide and hydrogen is passed under pressure of several hundred atmospheres over a heated catalyst consisting of a mixture of oxides, generally zinc and chromium oxides; reaction occurs and methyl alcohol can be condensed out of the final gases.

The action of various surfaces in promoting chemical action, especially combustion, is illustrated by the important work accomplished during recent years by Professor W. A. Bone of the Imperial College of Science and Technology at South Kensington.

Mr. Thomas Fletcher in 1887 showed that when a mixture of ignited gas and air is directed on to a large ball of iron wire

so as to heat it to the necessary temperature, and the current of gas is then momentarily interrupted, the ball will continue to glow with great increase of temperature, but without any sign of flame.

Bone began investigations in 1902 as to the influence of various hot surfaces on the combustion of hydrogen and carbon monoxide, and has arrived at the following general conclusions. (1) The power of accelerating gaseous combustion is possessed by *all* surfaces at temperatures below the igniting point in varying degrees, depending on their chemical characters and physical texture. (2) Such an acceleration of surface combustion is dependent on an absorption of the combustible gas and probably also of the oxygen by the surface, whereby it becomes activated (possibly ionised) by association with the surface; and (3) the surface itself becomes electrically charged during the process.

It also appears that while hot surfaces possess the power of accelerating gaseous combustion at temperatures below or near to the igniting point, the same power is manifested in an increasing degree as the temperature rises. And there is experimental evidence that the differences manifested by different surfaces at low temperatures practically disappear when the temperature of the surface reaches bright incandescence.

Incandescent surface combustion has been applied to a number of practical purposes, such as heating rooms and providing a hot surface suitable for many cooking operations such as grilling or roasting. It has also been applied on a large scale to raising steam, melting metals and alloys, and other practical purposes.

In the former case a diaphragm is prepared of granulated fire brick or other material bound together into a block and fitted into a suitable frame, which provides a space at the back into which the gas and air mixture can be fed (Fig. 54, p. 220). The gas being first turned on and lighted, air is then gradually added till a fully aerated mixture is obtained.

The flame soon becomes non-luminous and diminishes in size; a moment later it retreats on to the surface of the diaphragm, which at once assumes a bluish appearance. Finally, all signs of flame disappear and there remains an intensely glowing surface. The temperature thus attained is high enough even to melt platinum. Consequently in applying the principle to the construction of a furnace for fusion or other purposes in which a

high temperature is required the choice of the contact material is necessarily rather limited. Practically all solids except calcined magnesias and carborundum are excluded.

In raising steam three forms of apparatus may be adopted.

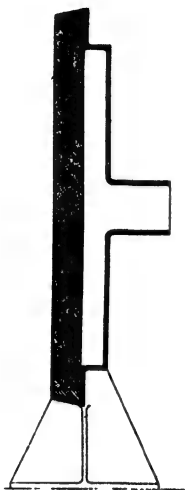


FIG. 54.
SECTION OF DIAPHRAGM FOR
SURFACE COMBUSTION (BONE)

In the case of a multitubular boiler in which the heating tubes pass through the body of the boiler containing the water, the tubes are packed with the refractory contact material in a granular state. The combustible mixture of air and gas passes through these tubes, and the control of the heat communicated to the boiler and the amount of steam raised, is effected either by adjustment of the amount of gas admitted or by working the tubes in groups, so that any number can be brought into action as required.

The diagrammatic section of an experimental boiler on this construction with ten tubes is shown in Fig. 56. The tubes are 3 feet long and 3 inches in diameter, fixed in a cylindrical steel shell

capable of withstanding a pressure of over 200 lbs. per square inch. Three only of the tubes are shown here. The gaseous mixture was forced through the tubes from a special feeding chamber attached to the front plate of the boiler; the products of combustion after leaving the boiler passed through a small heater containing nine tubes by which the water before entering the boiler could be warmed. The feed water on entering was at the temperature $5^{\circ}\text{--}5^{\circ}\text{C}$., or nearly 42°F ., on passing to the boiler the temperature was 58°C ., or about 136°F . The successful results obtained with this apparatus led to the erection of a boiler of about ten times its capacity by the Skinningrove Iron Company, Ltd., to be fired by the waste gas from an Otto by-product coking plant. The boiler is shown in the illustration. It consists of a cylindrical drum 10 feet in diameter and 4 feet from back to front, traversed by 110 steel tubes 3 inches in diameter packed with granular refractory material. In front of

the boiler is a specially designed feeding chamber which delivers washed coke-oven gas under a pressure of 1 to 2 inches of water. This gas with a regulated supply of air is drawn, by suction from a fan, through a short mixing tube, into each of the combustion tubes, where it burns without flame. The products of combustion pass outwards into a semicircular chamber at the back of the boiler, and thence to the tubular feed-water heater. The fan, which is attached just beyond this heater, is driven by

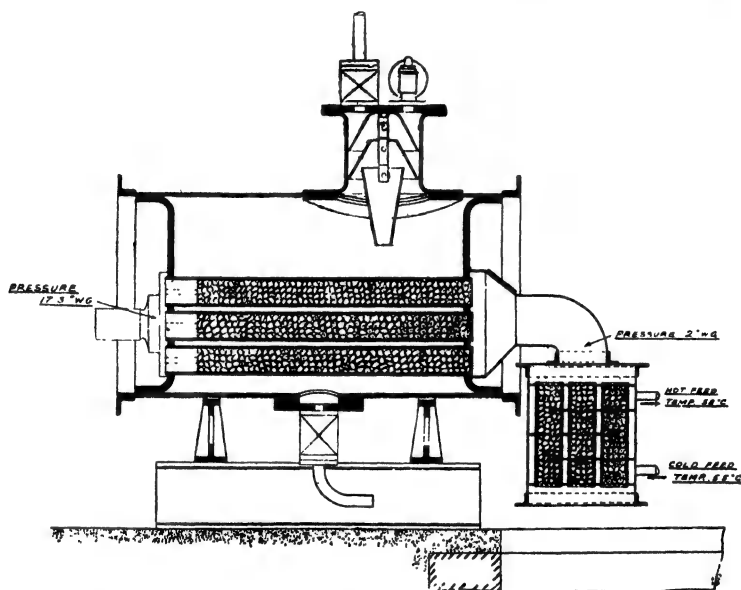


FIG. 56. EXPERIMENTAL TUBULAR BOILER FOR SURFACE COMBUSTION (BONE)

an electric motor, sucks out the cooled products at a temperature of 100°C . (212°F .) or under and discharges them into the atmosphere.

A second kind of arrangement provides for the use of liquid fuel in which the liquid is first burnt in a separate space under the boiler, and the imperfectly burnt products are carried with the requisite proportion of air through the tubes containing the granular contact substance.

In the third arrangement the granular material is placed in trays beneath the boiler.

The new method admits of the employment of almost any form of combustible gas, such as waste gases from the blast furnace or coke-oven, producer-gas of any kind, as well as water-gas and coal-gas. A high efficiency has been obtained—up to 92–94 per cent in the most favourable cases. In his recent Medal Address¹ to the Society of Chemical Industry (1933) Professor Bone spoke of the subject of surface combustion and described the results at Skinningrove as “an achievement which, for efficiency and concentration of evaporative power, broke all previous records and, so far as I know, has not since been surpassed.” Owing to the difficulty of obtaining suitable refractory material for packing the tubes, and trouble experienced with “back-firing” of the combustible gas, the “Bonecourt” boiler has not achieved the success which its efficiency merits.

The chapter began on the subject of catalysis and catalysts, but though it cannot be extended further the subject is by no means exhausted. Everywhere through the literature of chemistry, old or new, examples occur of processes which must be regarded as operating under the influence of these mysterious agencies. Hence to be exhaustive the whole known range of chemical changes would have to be reviewed.

There are many other cases in which a small quantity of a substance is sufficient to initiate or promote a chemical change otherwise not to be accomplished. These are to be found especially in connection with laboratory processes employed in the study of organic compounds. The remarkable characters and properties of enzymes will be described in a later chapter.

CHAPTER XIII

COLLOIDS

HUMAN existence hangs between two great worlds, the infinitely great and the infinitely little, and into both the chemist can penetrate. Though the mind fails altogether to grasp any clear idea of the space which separates us from any of the stars we can at least realise that it is enormous by a very simple reflection. As the earth travels round her orbit she sweeps out a

¹ *Journal of the Society of Chemical Industry*, 1933, p. 202 T.

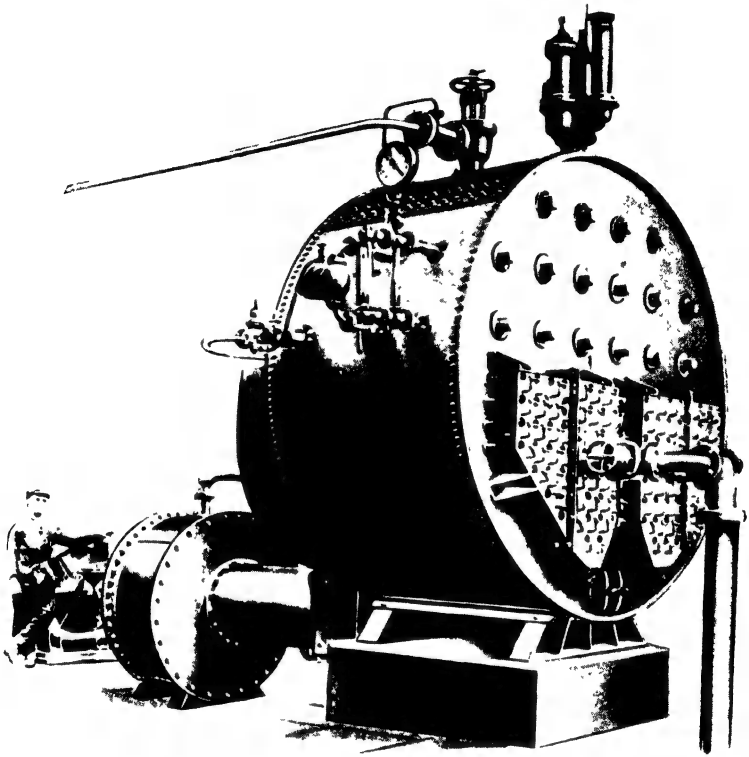


FIG 56 —BOILER WITH 110 TUBES AT SKINNINGROVE IRON WORKS
(BONECOURT SYSTEM)

circle more than 180 millions of miles in diameter. Nevertheless an observer who looks out into the night in summer and again in winter, or in spring and again in autumn, will be able to distinguish no change in the relative positions of the stars forming the constellations or patterns which they have for so many ages written on the background of the sky. And when we remember that though modern instruments are capable of appreciating differences far more minute than any which the unaided eye can trace, the vast majority of stars remain apparently unaltered in position when viewed from opposite sides of the earth's orbit. Into these vast spaces the spectroscope, brought into use as a practical instrument just over seventy years ago, has enabled the astronomer and the chemist to penetrate and to investigate the composition as well as the motions of these distant sources of light. The result has been to show that the elements which enter into the composition of the earth, the seas, and the atmosphere of our planet, are to be found everywhere in the most distant regions of space. They are not equally distributed, for in one star hydrogen, for example, may be found to be present, while in another the lines indicating that element are absent, and similar concentrations of calcium and magnesium, iron, sodium, and the rest may be recognised in stars and nebulae.

This, however, is not the direction in which attention must be concentrated in these pages. The reader who is interested in astro-physics or astro-chemistry must consult one of the numerous treatises on the subject, from which he may learn something of the progress which has been made in spectroscopic investigation concerning the composition of our sun and the stars, which are believed to be constituted like our sun, as well as the nature of comets and nebulae. It is sufficient to say that the results of late years have been to some considerable extent employed in connection with theories concerning the origin and evolution of the elements.

Systematic and quantitative chemistry is based on the assumption that matter is not divisible *ad infinitum*. It is known to the senses in the form of masses, the most minute of which, discernible by sight, contain many millions of the ultimate particles—molecules or atoms—which are subjects of study by the physicist and chemist. This is true even of the granules, which, produced by the subdivision of ordinary massive matter, are large enough to be just visible under the highest powers of

the ordinary microscope. Particles which are too small to be seen by the eye alone or assisted by lenses may be perceived by other senses, especially by smell. Everyone has heard of the grain of musk which, lying for years on the pan of a balance, continues to emit its characteristic odour without betraying any loss of substance by appreciable loss of weight. And yet there seems no reason to doubt that the effect on the olfactory surface is produced by contact with the minute particles of musk substance which enter the organ. The sense of smell, like that of taste, depends on actual contact of the sensory surface with the exciting substance, and it does not appear to depend like the faculties of hearing and of sight on the entrance of impulses in the nature of waves of air or of "æther" into the receiving nervous surface. The extremely minute division of matters capable of exciting smell may be inferred from common observations in everyday life. One of the commonest experiences of a walk in the country is the smell of burning weeds. When the vegetable matter thus disposed of is heated it is partly consumed by the aid of the oxygen of the air and is converted into vapours of water and carbon dioxide which are inodorous. At the same time a portion, but only a very small proportion, of the stuff is by the heat alone, without combustion, made to yield substances such as acetic acid and phenols, which in a state of vapour are acrid and disagreeable to the nose and eyes. They are perceptible at great distances when diffused through the air. They can be smelt when the accompanying smoke is no longer visible and at a distance of half a mile or more. The matter thus diffused would probably not exceed an ounce or two, but it can be recognised when spread in this way through millions of cubic yards of air. One is tempted almost to believe that under such circumstances the sense may be awakened by separate molecules arriving singly or a few at a time.

The subdivision of matter in its less extreme forms may, however, be rendered perceptible by the eye if only the illumination is sufficient. The passage of a sunbeam through a room in which nothing could previously be perceived is enough to show that the apparently clear air is filled with myriads of particles which by reason of their small size remain suspended. These little particles are, however, relatively monstrous, for they consist of minute hairs, pollen, yeast cells, animal and vegetable débris of all kinds, each of which possesses an organic structure, mixed

with tiny grains of sand or earthy matters blown up by the wind. This process of illumination will help to reveal other effects in which the actual masses of the particles can be calculated. If one of the artificial colouring matters such as magenta, fluorescein, or eosine, of which the composition and molecular weight are known, be dissolved in water the solution may be diluted till it contains no more than 1 or 2 parts of the solid in 100 millions of the liquid, and the colour will still be perceptible. When the solution possesses the property of fluorescence which is beautifully shown by fluorescein and by eosine, this effect is still perceptible when the dilution is 20 million times greater, provided the liquid is examined by the aid of a converging beam from an electric arc directed into the body of the liquid. It can be shown that the particles thus made recognisable are still not resolved into separate molecules, for the dilution would still require to be increased some seven or eight thousandfold before the dissolved substance is reduced to one molecule per cubic millimetre.

Another illustration of minute division, even into separate atoms, has been described in connection with radio-active substances, the escaping atoms making themselves perceptible by their electrical effects and by exciting phosphorescence on certain surfaces. Each atom as it strikes the screen of the spinthariscopes produces a separate vivid spark.

The observation of minute particles, approaching molecular magnitudes in some cases, has been accomplished within recent years by the use of the instrument known as the "ultra-microscope." It has long been recognised that however intense a beam of light from the sun or electric arc may be, it remains invisible until it strikes some surface. It is then scattered more or less, and if any of the scattered rays reach the eye they produce the sensation of vision. Hence the course of a beam of sunlight traversing a room containing dust-laden air is visible, but if the same beam be transmitted through a glass tube or other vessel in which the air has been purified from suspended particles the course of such a beam will be imperceptible. In the ultra-microscope¹ advantage is taken of these facts. The medium holding minute particles diffused through it is examined through a high-power microscope, while a strong beam of light,

¹ The ultra-microscope was invented by H. Siedentopf and R. Zsigmondy early in the present century.

admitted through a very fine slit, is cast through the space in front of the object glass. As the axis of the microscope is vertical while the beam is horizontal it is obvious that no portion of it enters the microscope directly. Hence if anything is seen it is the little rays reflected sideways from the surface of the particles under examination. The image observed therefore depends on the power of the microscope and the intensity of the illumination. The size of the particles inspected cannot be observed directly, but only inferred from a knowledge of the amount of solid contained in a known bulk of the liquid and the number of particles which can be counted in a measured space.

Ordinary microscopes may give a magnification amounting, under favourable circumstances, to as much as 3000 diameters, and so render visible objects which have a size represented by about one ten-thousandth of a millimetre across. The ultra-microscope is said to be capable of distinguishing objects having a diameter one-tenth of this with light from an arc lamp, and considerably smaller when illuminated with the brightest summer sun. These minute measures are usually indicated by the symbols μ and $\mu\mu$ which stand respectively for one-thousandth and one-millionth of a millimetre.

It is estimated that the diameters of gaseous molecules must lie somewhere between 0.1 to 0.5 $\mu\mu$. Hence there appears little probability of ever rendering these visible, for the finest particles discernible in suspension have a diameter equal to 0.01 μ or 10 $\mu\mu$. But though separate individual molecules may never be revealed to mortal eye, observations on some of these very small particles afford a vision which gives a lively stimulus to the imagination.

It has long been known that very small particles of any solid when suspended in water are seen under the microscope to be in a state of movement. This has no relation to the composition of the solid, but is dependent solely on the size of the particles which must not exceed 3 μ in diameter. The movement was observed originally by Dr. Robert Brown, the botanist, in 1827-8, and hence is commonly referred to as the Brownian movement. The cause of it was long doubtful, but there seems to be now a reasonable explanation which is generally accepted.

For the study of these movements it has been found convenient to prepare certain suspensions formed when alcoholic

solutions of resin or similar substances are mixed with a large volume of water. The resin being insoluble, or but slightly soluble in water, is thrown out in the form of minute spherical drops, of which the greater part remain for a long time in suspension. Gamboge is a resin familiar as a water-colour pigment which lends itself to this process very suitably, though other resins such as mastic or even common resin will also answer the purpose. A number of these systems and other imperfect solutions have been the subject of numerous experiments during the last twenty years or more. These liquids contain granules in suspension so small that they commonly pass through ordinary filter paper, and the liquid can only be clarified by resort to special processes. When allowed to rest undisturbed for a long time the upper layers of the liquid gradually become clear, while the floating particles accumulate in regularly increasing proportion in the lower layers. When such a liquid is examined under the microscope the granules are seen to be all spheroidal in form and to vary considerably in size, though after the deposition of the coarser particles no solid can be discovered by the unaided eye. They can be most conveniently sorted by submitting the liquid to the action of a centrifuge, the larger masses passing first toward the periphery. This method was introduced by Professor Jean Perrin of the Sorbonne, who has given much attention to the size of particles which exhibit the Brownian movement. A method which has been used for several similar purposes is based on the formula given by the late Professor Sir George Stokes for the velocity of a small sphere of known density falling through a medium of which the viscosity is known. With a system holding in suspension grains of uniform size the rate of fall can be easily measured by observing the time occupied while the top layer of known depth becomes clear.

Another process is to count under the microscope the number of granules in a very small but known volume of a suspension containing grains of uniform size, whereof the total mass is known.

In the case of gamboge the diameter of the granules was found, by the first method, to range from $.90\mu$ to $.42\mu$, and by the second from $.92\mu$ to $.42\mu$. The last result involved the counting of about 11,000 grains.

The main result arrived at by Perrin is the conclusion that the Brownian movement of small particles in suspension and the

movement of molecules are of the same type and are due to the action of the same forces. These forces appear to be the translatory forces of the moving molecules of surrounding water ; in other words the granules in suspension are pushed about by the molecules surrounding them. In order that movement may result from contact with a molecule the particle must be small.

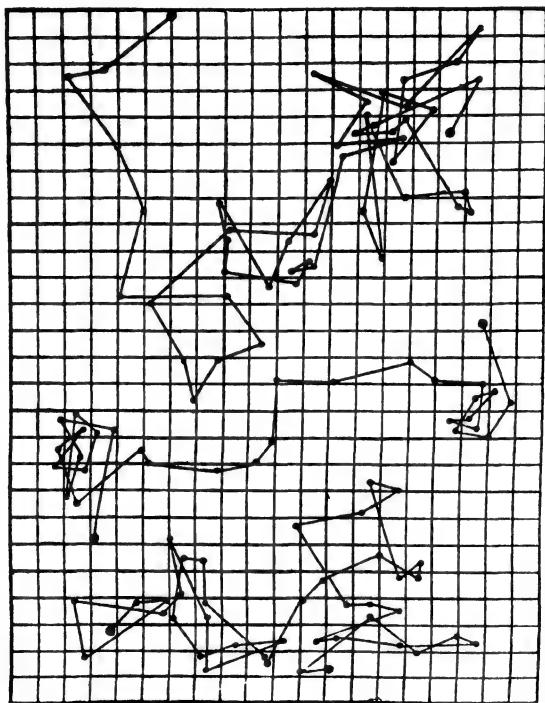


FIG. 57. BROWNIAN MOVEMENT
Paths of three separate granules

The Brownian movements executed by the granules may therefore be supposed to be very similar to those of the molecules themselves. An idea of their character may be gained from the adjoining figure which was obtained by observing the positions of three granules every 30 seconds. These positions are then joined, in the diagram, by straight lines.

Investigations of the kind just described have assumed a position of great interest and importance within the last few years ;

by means of them Perrin was able to show that a gram molecular weight of any substance contained about 6×10^{23} individual molecules. On the basis of this result a single atom of hydrogen weighs approximately 1.6×10^{-24} gram: the small magnitude of this value is quite beyond our comprehension. The weights of the atoms of other elements may be obtained by multiplying that for hydrogen by the atomic weight of the element under consideration.

Something is at last beginning to be understood regarding the constitution of that peculiar state of matter to which the name "colloid" has been given. To Thomas Graham (at one time Professor of Chemistry at University College, London, and later Master of the Mint) we owe the first and very important researches concerning the diffusion of dissolved substances. The first memoir on the subject is the Bakerian Lecture to the Royal Society for 1849. In the course of these experiments Graham discovered not only that dissolved salts and other compounds *diffuse*, that is, they move from place to place in the liquid, with various degrees of rapidity, but that the same compounds are divisible into two main classes according as they possess or do not possess the power of passing when in solution through animal membranes or parchment paper. These two classes Graham called "crystalloids" and "colloids." The former includes not only substances like salt and sugar which are capable of crystallising, but compounds such as hydrogen chloride (hydrochloric acid) which were not known in the crystalline state. These substances diffuse through membranes with various degrees of rapidity. The other class, colloids, are typified by gelatine or glue (κόλλα, glue).

The classification of substances into crystalloids and colloids has now been discarded, since under suitable conditions a given substance may be obtained in true solution as well as in the quasi-solution characterised by the name colloid. It is the practice at the present time to speak of the "colloidal state," which almost any substance may assume. This state is associated with certain physical properties, some of which will be described shortly, and is attributed to the presence of particles too small to be seen in the microscope yet larger than the single molecules which exist in true solution (see p. 170); it is the heterogeneous nature of colloidal systems which gives them their characteristic

properties and accounts for their inability to diffuse through membranes.

Colloids are not all of organic origin but are obtained by a great variety of processes from salts, oxides, and even metals which under ordinary conditions are practically insoluble in water. An example or two will make the matter clear. Silica SiO_2 is known in the form of rock-crystal, quartz rock, agate, carnelian, opal, cairngorm, flint, and other stones, sometimes nearly pure as in rock crystal, more usually coloured by the presence of small quantities of ferric and other oxides. These agree in being practically insoluble in water, but if melted with caustic soda or merely boiled for some hours with a solution of the same the silica is rendered soluble, and a moderately strong solution of the product in water constitutes the "water-glass" of the shops. If a diluted solution of water-glass is poured into an excess of dilute hydrochloric acid no precipitate is formed and the solution remains clear. It contains silicic acid, a colloid, together with the sodium chloride which has been formed and the excess of hydrochloric acid, in true solution. By pouring the liquid into a bag of parchment paper and suspending it in water the latter substances diffuse away, and if fresh water is supplied several times in place of the diffusate a liquid is ultimately left within the bag which contains the whole of the silicic acid with mere traces of the chlorides; this process of separating substances in true solution from the colloid is known as "dialysis." The residual liquid is clear as water, it may be concentrated by evaporation, provided no solid crust is allowed to be formed at the sides of the dish, till it flows like syrup, and ultimately it will dry up into a glass-like mass. The dissolved substance exhibits extremely small osmotic pressure and neither reduces the freezing-point of water nor raises the boiling-point. The liquid is, however, very sensitive to the presence of small quantities of salts and acids and speedily sets into a gelatinous mass when any electrolyte is added. The pseudo-solution of silicic acid thus obtained, called by Graham a "colloidal solution," is now simply called a "sol," while the gelatinous mass resulting from slow change or the addition of saline substances is called a "gel."

By similar processes which involved the preparation of the colloid form and its purification from the attendant crystalloids by the method of dialysis through a membrane, Graham

succeeded in preparing sols of the hydroxides of iron, chromium, and aluminium, tungstic acid and other substances. Some of these preparations may be made by other methods. Thus aluminium hydroxide (hydrated alumina) may be obtained in the form of a sol by making first a solution of aluminium acetate and then boiling the solution in an open dish till the acetic acid produced has been completely driven off. Water must be added from time to time to replace that which is lost by evaporation. The residual hydrous alumina is the basis of the aluminous mordant used in calico printing.

A very interesting sol is produced by boiling white arsenic (arsenious oxide As_2O_3) in water and adding hydrogen sulphide to the solution. A bright yellow colour is immediately developed but no precipitate is formed, although arsenious sulphide, As_2S_3 , is insoluble in water. If now a few drops of hydrochloric acid are added to the clear liquid a yellow precipitate of the sulphide is immediately formed, and after it has had time to subside the liquid is seen to be colourless.

The most remarkable sols, however, are those which are producible from certain metals, especially those which have been so long called the "noble metals," namely gold, silver, and platinum.

Faraday discovered in the earlier half of the nineteenth century that a solution of gold chloride on which is floated a solution of phosphorus in ether will yield a liquid of various colours, blue, violet or rose according to circumstances. A mixture of tin salts added to a solution of gold also yields the purple of Cassius which is long retained in suspension. The most beautiful ruby glass also owes its colour to gold which is certainly in the metallic state, not only on account of the fact that the temperature of melting glass is far above that at which all known compounds of gold are decomposed, but the particles have been examined by the ultra-microscope and are known to be for the most part spherical. Some of the coloured liquids just mentioned must have been known to the alchemists, and it is not improbable that one of them was an ingredient in the "elixir," the composition of which was their chief subject of study. "Soluble gold," which was actually used in medicine down to the end of the seventeenth or beginning of the eighteenth century, probably consisted of one of them.

To prepare a coloured solution or pseudo-solution of gold it is only necessary to add to a weak solution of the chloride in water

any one of many easily oxidisable substances or as they are called "reducing agents." Phosphorus has already been mentioned, but phosphorous and sulphurous acids, essential oils of various kinds, formaldehyde, sugars, hydrazine, hydroxylamine and many other substances have been used. The colour produced depends on the agent used. Thus when a weak solution of pure chloride of gold is exposed to contact with carbon monoxide gas bubbled through it, a *red* colour is produced which is pretty stable, and the hydrochloric acid which is left in the liquid as a consequence of the deposition of the gold can be removed by dialysis.

If the same gold chloride solution is neutralised very carefully by means of a weak solution of sodium carbonate and a very dilute solution of hydrazine hydrate is added drop by drop a *blue* liquid is formed. And further, according to A. Gutbier, the same reducing agent added to the same gold chloride solution in successive portions is capable of producing several colours successively. If a very weak solution of gold chloride is mixed with a few drops of a very weak phenylhydrazine hydrochloride solution a red colour is first produced, a little more of the reagent produces a violet colour, which with the addition of further quantities becomes bluish and ultimately deep blue. The colour of the sol depends on the size of the particles present; if they are relatively large the colour will be towards the red end of the spectrum, whereas small particles give colours approaching the blue and violet.

These coloured liquids are producible in a very curious manner by electrical dispersal of the metal itself below the surface of water or other liquid. By making a small electric arc between gold wires under water purple-red clouds and a coloured liquid result from dispersal of the metal which comes from the cathode only

A remarkable and characteristic property of the particles of a colloidal system is that they always carry an electrical charge, either positive or negative; as a result they are able to move under the influence of an electric current, or as the early workers looked at it, they are attracted or repelled from one electrode or another. The movement of colloidal particles in the electric field has been examined by Messrs. Linder and Picton, who began their researches so far back as 1892, and who must be regarded as among the chief pioneers in this difficult field of

enquiry. They describe the electrical convection of arsenious sulphide as follows, using the yellow liquid in which no particles are visible under the microscope, while the liquid is filterable :

“ The resistance of such a solution is extremely high and the current passing through it in one case amounted to only 0.000007 ampère. The conductivity is probably due to the presence of small traces of arsenious oxide ; but, however that may be, the passage of this small amount of current is accompanied by the repulsion of the colloidal sulphide as a whole from the negative electrode.” (*Trans. Chem. Soc.*, 1897, p. 569.) They also observed that of different colloids examined some are positive and some negative : thus arsenious sulphide is negative in a solution faintly acid to litmus, while ferric hydroxide is positively charged under the same conditions.

This property of migrating under the influence of an electric current, known as *cataphoresis*, has been utilised commercially. In a suspension of china clay the particles are of colloidal character, and they can be made to move *en masse* towards one of the electrodes ; in this way the process of drying the clay can be greatly expedited. Another recent development is the so-called “ electrodeposition ” of rubber, which depends on the same principle. The colloidal particles in the rubber latex (see chapter XXV) are negatively charged and so move to the anode and deposit there under the influence of an electric current ; by varying the contour of the anode articles of any desired shape can be made.

All these hydrosols or colloidal solutions are coagulated when mixed with an electrolyte. It has already been mentioned that the addition of a little hydrochloric acid to the arsenious sulphide liquid causes immediate precipitation of the solid sulphide, but an acid is by no means necessary, as in most cases any soluble neutral salt will bring about the same effect. The precipitating or coagulating effect of electrolytes on colloids has some important consequences. Many rivers contain clay and similar particles in colloidal suspension which are carried down towards the sea ; when the saline water is encountered the salts present, chiefly sodium chloride, bring about precipitation of the suspended particles so that in the course of time the huge deposits, known as deltas, are formed. The use of aluminium sulphate for the clarification of water for drinking purposes (see chapter XVI) also depends on the precipitation of colloidal particles.

It is interesting to notice that the coagulating effect of electrolytes is delayed or prevented altogether in some cases by the protective effect of mixing the hydrosol with one of the more stable colloids, such as a solution of gelatine. Faraday discovered, for example, that his red gold solution when mixed with jelly "is rendered much more permanent than before; and then it may by a little warmth be had in the fluid state, or by cooling as a tremulous jelly, or by desiccation as a hard ruby solid, presenting all the transitions between the gold fluid and the ruby glass." (Bakerian Lecture, 1857.) It is probable that the presence of organic materials, capable of exerting the protective effect, is responsible for the maintenance of clay particles in the colloidal state in many rivers which eventually form deltas.

Hitherto it has been tacitly assumed that all colloidal solutions have similar properties, but this is not strictly true, since it is possible to divide them up very roughly into two groups according to their sensitivity to electrolytes. Those which are very easily precipitated are called *lyophobic*, that is "liquid hating," whereas others much more difficult to coagulate are termed *lyophilic*, or "liquid loving." The colloidal metals, sulphides, hydroxides, and other compounds of metals, generally belong to the first group, and the organic colloids, such as gelatin, agar-agar, albumin and starch fall into the latter category. These organic substances form molecules of great complexity and become even more complex by taking up molecules of water, so that they eventually become large enough to acquire the properties of a colloidal rather than a true solution; actually they behave as something in between the two extremes. It appears, therefore, that in lyophilic systems each particle may be regarded as being a complex molecule; some support for this view is obtained from estimates of the molecular weights. Experiments on the diffusion of various colloids by Herzog and Kasarnowski in 1908 led to the following figures, which are of course only approximations and are to be compared with the molecular weight of hydrogen as 2.

Substance.					Molecular weight.
Egg albumin	17,000
Pepsin	13,000
Invertin	54,000
Emulsin	45,000

More recent estimates have given even larger values, thus :

Substance.	Molecular Weight.
Gelatin . . .	10,000 to 70,000
Egg albumin . . .	34,000
Serum albumin . . .	67,000

Calculating the molecular diameter of such bodies the largest molecules reach the size represented by $10\mu\mu$, which brings them within the range of colloidal systems.

The study of colloids is of theoretical interest because it shows how the gap between true molecular solutions, exerting definite osmotic pressure, and the suspensions or emulsions containing particles visible to the naked eye, or in a microscope, can be bridged. There is, however, also the practical side because colloidal systems are so widely encountered ; the living organism is a mass of colloids, and it has been suggested that many biological phenomena can be attributed to this fact. The importance of colloids in connection with the clay and rubber industries and the purification of water has been mentioned, but there are very many more applications, and no one interested in chemistry can afford to neglect a close examination of the subject.

PART III
MODERN APPLICATIONS OF CHEMISTRY

CHAPTER XIV

HYDROGEN

UP to the middle of the eighteenth century several gases were known which were confused together under the general name "inflammable air." But in 1766 Henry Cavendish, in a paper on "Factitious Air," showed that the gas which is procured by the action of diluted sulphuric or muriatic acid on zinc and iron is to be distinguished from the inflammable air known as marsh-gas, and the other variety obtained by passing air over or through red-hot charcoal. He afterwards proved that this kind of "inflammable air" unites with half its volume of "dephlogisticated air" (oxygen) to form water.

The inflammability of the gas coupled with its extraordinary lightness led the discoverer and others to suppose that it was actually "phlogiston" itself, the then assumed hypothetical principle of combustibility. The name hydrogen, which means water producer, was given to the gas by Lavoisier, in accordance with the system of nomenclature contrived by him some years later. The lightness of the gas always excited curiosity, and after the phlogistic theory had been abandoned and phlogiston a thing of the past, the idea arose that hydrogen was in fact a realisation of the notion which had come down from ancient times as to the existence of a *πρώτη ὕλη* or protyl, the primal matter out of which all else was composed.

The development of the balloon into the airship is one, although not the chief, reason for enquiry into the methods by which hydrogen may be manufactured in quantity. Formerly aeronauts were content with charging their balloons with an impure kind of methane, obtained by distilling coal at a relatively high temperature, and collecting the last portions of the gas escaping from the retort. This gas is about eight times as heavy as hydrogen.

The difference of density, however, is so great that gas of this quality does not satisfy the modern requirements. Not that it

is by any means necessary to secure chemically pure hydrogen, as the proportions of the ordinary impurities, such as sulphuretted hydrogen, arseniuretted hydrogen, and the vapours of volatile hydrocarbons, or a little carbon monoxide are so small as to exercise but little influence on the density, and hence the lifting power of the gas. The chief objection to the presence of such impurities as sulphuretted hydrogen is that they slowly oxidise into acids which are apt to destroy the fabric of the balloon.

The German airship *Graf Zeppelin* has a gas capacity of about 3,700,000 cubic feet, and this volume of hydrogen at a temperature of 0° C. (the freezing-point of water) and a pressure of 1 atmosphere (15 lbs. per square inch of surface), would weigh nearly 9 tons. Air is nearly $14\frac{1}{2}$ times heavier than hydrogen, consequently the same bulk of air, under the same conditions, weighs about 130 tons. The lifting power of such a volume of hydrogen gas would therefore be about 120 tons. The ill-fated British dirigible *R101* and the United States vessel *Macon* had even larger lifting power, and the new airship being built in Germany, with a capacity of nearly 7 million cubic feet, should be able to lift over 200 tons. When the frame of the balloon, the car, the engines, the fuel, and the guns, if any, are allowed for, it is obvious that the machine is still capable of carrying a considerable number of men and bombs or other cargo. But it must be remembered that when the airship leaves the ground it rapidly rises into regions in which the pressure is very much less than 1 atmosphere, and the gas expands, and if closely confined would probably burst the envelope. This effect is at high elevations counteracted to some extent by the reduction of temperature. Some of the gas would, however, escape through a relief valve, and on descending would probably have to be replaced by means of a reserve of compressed gas carried in the car.

The airships, however, are commonly provided with a second envelope containing air into which the exhaust gases from the engine are delivered for the purpose of regulating the temperature of the hydrogen, warming it when the ship has risen to such a height as to be exposed to considerable cold. It is also important to observe that the materials of the envelope, which consist of a strong double cotton cloth enclosing a thin layer of rubber, are not impervious to hydrogen gas, and that in course of hours an appreciable escape occurs by the process of diffusion. All these

facts make the available carrying power of any sort of balloon less than the amount calculated from the volume of hydrogen with which it is charged at starting.

The chief chemical applications of hydrogen are in connection with the production of ammonia from atmospheric nitrogen (chapter XXVII) and the hardening of fats; for the latter process hydrogen of a high standard of purity is required owing to the danger of poisoning the nickel catalyst (p. 215). It is likely that in the near future considerable quantities of hydrogen will be required for the large scale hydrogenation of coal and creosote for the production of fuel for internal combustion engines; this subject will be discussed in a later chapter. Mixed with carbon monoxide hydrogen is the raw material for the new catalytic processes for the manufacture of methyl and other alcohols.

A small quantity of hydrogen is also used in the remarkable "atomic hydrogen" blow-pipe invented by Dr. J. Langmuir; a stream of hydrogen gas is passed through an electric arc between two electrodes of tungsten. The molecules of gas are split up into atoms and in the flame where the gas burns, just beyond the arc, a very large amount of heat is liberated, partly due to combustion of the hydrogen but mainly to the heat evolved in the re-combination of the hydrogen atoms to form molecules. The atomic hydrogen flame reaches a temperature of nearly 3800°C. , and is used for welding steel, nickel, and aluminium; it is hot enough to melt molybdenum and tungsten.

Other uses of hydrogen, in the form of the ordinary type of blow-pipe, are the melting of platinum, the working of fused quartz in making apparatus of silica, the autogenous soldering of lead sheet, and the making of joints in lead pipes employed in chemical works. The latter are found to resist corrosion by acids much more successfully than when solder is used.

We may now review the principal methods by which hydrogen may be obtained, and from a consideration of the materials and conditions of each some conclusion may be arrived at as to their practicability from the industrial point of view.

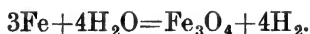
We may at once exclude those processes which are too costly or otherwise objectionable, such as the action of metallic sodium on water or the dissolution of metallic aluminium in caustic soda. These are frequently resorted to in the laboratory, but are unsuitable for use on a large scale.

The available methods may be ranged under several heads as follows :

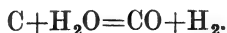
1. The action of metals on acids.
2. The action of metals on steam at a red heat or on water.
3. The action of carbon on steam at a red heat.
4. Electrolytic processes.
5. Miscellaneous methods.

1. *Metals and acids.* The traditional laboratory process for making hydrogen by the action of diluted sulphuric acid on zinc cannot be considered, as the cost of the zinc would be far too great. The only metal by which it could be replaced is iron, but inasmuch as 28 parts by weight of iron are required to produce 1 part by weight of hydrogen, the mere mass of material would be an objection. One ton of iron would require 3920 pounds or $1\frac{3}{4}$ tons of sulphuric acid, and would produce only 13,917 cubic feet of gas, a quantity which would be about one-twentieth of the capacity of a small balloon. The action of metals on acids may therefore be at once ruled out of the practicable processes for generating hydrogen for industrial purposes.

2. *Decomposition of water by metals.* The action of red-hot iron on steam results in the production of hydrogen gas and a residue of magnetic oxide of iron.



In this case iron theoretically yields one-third more hydrogen than when it is made to act on sulphuric acid. By associating with this process another for the restoration of the oxide of iron to the metallic state, and working the two alternately, a plan for the production of hydrogen on a practical scale results. The reduction is most advantageously effected by means of water gas, the product of the action of steam on coke at about $1000^\circ \text{C}.$,

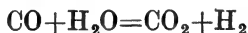


The equation indicates that theoretically the interaction should result in the production of equal measures of carbon monoxide and hydrogen gases, but actually carbon monoxide is somewhat below the theoretical amount, a small quantity of carbon dioxide being formed by the intrusion of a little air, the oxygen of which is of course accompanied by four times its bulk of nitrogen. These operations have been the subject of numerous patents.

The most successful form of the iron-steam method for making hydrogen is that known as the Lane process, in which the iron is obtained by the reduction of its oxide, in the form of burnt iron pyrites or of an iron ore. This reduced material is heated to about 700° C. in vertical retorts and steam blown in ; the oxide formed is regenerated by means of water gas.

3. *Decomposition of water by carbon.* The hydrogen contained in water gas to the extent of about half its volume may be secured by the comparatively simple process of freezing out the attendant impurities. These consist of a nearly equal volume of carbon monoxide, together with 2-5 per cent of carbon dioxide, and about the same bulk of nitrogen and traces of hydrocarbons and of sulphuretted hydrogen. The boiling-point of hydrogen being about -253° C., it boils at some sixty degrees below the boiling-point of nitrogen (-196°), oxygen (-183°), or carbon monoxide (-190°), and consequently when cooled by liquid air under a moderate pressure these impurities are liquefied and removed, while the hydrogen retains the gaseous state. A somewhat similar process is said to be in use in Germany for separating hydrogen from coke-oven gas, which consists of hydrogen, carbon monoxide and certain hydrocarbons, such as methane, which are not very difficult to liquefy.

Most of the hydrogen in use at the present time is probably made from water gas, but a chemical and not a physical method is used to separate it from carbon monoxide. The water gas is mixed with steam and passed over a catalyst, generally an oxide of iron, at a temperature of about 400° C. ; the following reaction occurs :



that is the carbon monoxide is converted into dioxide (CO₂) and hydrogen. The gas is thus enriched by hydrogen and the carbon dioxide is readily removed by dissolving it out with water under a pressure of 25 atmospheres ; traces of carbon monoxide remaining are absorbed by means of a solution of a copper (cuprous) salt containing ammonia.

4. *Electrolysis.* Hydrogen is liberated in several operations as a by-product which till recently has had but little value. In the processes for the manufacture of caustic soda by the electrolysis of brine, and in the large-scale method for the production of metallic sodium, by electrolysis of fused caustic soda, hydrogen is liberated. But these two methods are necessarily

associated with the caustic soda and sodium which are of greater value, and to collect the gas a compressing plant would be required.

The pure hydrogen required for the hardening of fats is usually made by the electrolysis of a dilute solution of sulphuric acid, but for general purposes this is not an economic method. At the Second World Power Conference, held in Berlin, in 1931, Colonel G. P. Pollitt of the Imperial Chemical Industries Ltd., is reported as having said that the electrolytic production of hydrogen can only compete with that made from water gas, by the chemical process just described, if electric power is available at the cost of 0.05 pence per kilowatt-hour, or less. This is an extremely low price for electricity, about one-tenth of that generally charged for power in Great Britain, and so the electrolyte manufacture of hydrogen is only possible where the availability of water power makes electricity very cheap. In such places, for example in parts of North America and on the continent of Europe, electrolytic hydrogen is actually used for the production of ammonia.

The hydrogen obtained by any electrolytic process is apt to be accompanied by small quantities of oxygen, while the oxygen simultaneously set free is liable to contain a little hydrogen which in certain cases would be objectionable or even dangerous; special care is therefore taken to avoid any possibility of the gases mixing.

5. *Miscellaneous methods.* Some of these are designed to furnish the means of generating hydrogen in moderate quantities in the field by requiring only simple and portable apparatus. One substance proposed for this purpose is impure calcium hydride, CaH_2 , a white powder to which the name *hydrolith* has been given. It is produced under a French patent. When mixed with water about one cubic metre of hydrogen is evolved from one kilo of the material, and this costs five francs.

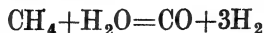
Hydrogenite is the name given to another material in which ferrosilicon is mixed with a relatively large quantity of caustic soda and some lime. When heated this mixture evolves hydrogen and leaves a mass of silicates of sodium and calcium. Ferrosilicon in fine powder also dissolves in a solution of caustic soda to give off hydrogen; this is the basis of the *silicol* process.

When acetylene is heated it readily breaks up into its constituent elements, hydrogen in the form of gas and finely divided

carbon. As acetylene is produced pretty cheaply from calcium carbide this principle has been made the subject of a patent. The gas contained in steel cylinders is decomposed by electric sparks, and the very fine carbon deposited is valued for making printer's ink. The process has been used at the Zeppelin factory at Friedrichshafen, but it appears not to be entirely free from danger, as it is said that explosions have occurred.

Another process involving a somewhat similar principle is now in the course of active development in order to find an outlet for some of the ammonia being produced in excess of the demand for agricultural purposes. When the gas from a cylinder is passed through a special "cracking" apparatus containing a heated metal catalyst, the ammonia decomposes into a mixture of three parts of hydrogen to one part of nitrogen; for most purposes the presence of the latter is not detrimental. It may seem absurd, at first sight, that ammonia made from hydrogen should subsequently be split up in order to reform the hydrogen, but the explanation of the method used lies in the lower transport cost of the ammonia. The Imperial Chemical Industries Ltd., issue a pamphlet describing the production of hydrogen from ammonia in which it is stated that "the contents of one 100 lb. cylinder of ammonia will produce 4,500 cubic feet of pure hydrogen. To transport this quantity of hydrogen in cylinders it would be necessary to carry sixteen times the weight of the metal in the one ammonia cylinder."

In conclusion mention may be made of a method for obtaining hydrogen from the gas issuing from petroleum wells, which consists mainly of methane (CH_4). The process is being worked by the Standard Oil Company of New Jersey, U.S.A., where a plant capable of making 300,000 cubic feet of hydrogen per hour is said to have been erected. The methane is mixed with steam and passed over a catalyst, iron or cobalt together with aluminium oxide supported on clay, at about 1000°C ., when the reaction:—



takes place. The resulting gas, containing excess of steam, is then passed over another catalyst at a lower temperature, as in the removal of carbon monoxide from water gas; the carbon dioxide and traces of monoxide remaining are then removed as already described.

CHAPTER XV

OXYGEN AND NITROGEN

EVERY schoolboy is acquainted with the process, common a few years ago and still used on a small scale for producing oxygen gas, by heating potassium chlorate, either alone or mixed with a small quantity of manganese dioxide. Priestley's original method of heating mercuric oxide (red precipitate) is described in most chemical textbooks, as well as the decomposition by heat of a considerable number of peroxides and other metallic oxides, and highly oxidised substances such as potassium permanganate, bleaching powder, sulphuric acid. But for industrial purposes and manufacture on a fairly large scale, a process was introduced, by patent in 1880, by MM. Brin frères which soon took the place of all the others and became established as a successful commercial undertaking. This was based on the fact that at a low red heat barium oxide in a stream of air, deprived of carbon dioxide, is converted into barium dioxide, $\text{BaO} + \text{O} = \text{BaO}_2$. The latter compound heated to a higher temperature gives off again the absorbed oxygen, while barium monoxide, baryta, BaO , is reproduced.

The inconvenience of alternately raising and lowering the temperature of the retorts in which the baryta was heated, and the wear and tear involved in these operations, led to the substitution of change of pressure for change of temperature with great advantage.

An apparatus was devised in which, by means of automatic reversing gear, the air could be alternately introduced into the retorts under slight pressure, and after absorption of the oxygen and escape of the nitrogen, the oxygen could be pumped off by reducing the pressure below atmospheric, but without altering the temperature of the retorts and their contents. Oxygen made by this process had a purity of 93 to 96 per cent. Owing to recent developments, however, the Brin process is now obsolete.

Oxygen always accompanies the hydrogen made by the electrolysis of aqueous solutions, but the gas obtained in this way is usually wasted, unless it is required for some purpose close to

hand. It is said to be unprofitable to collect and compress it for sale, presumably because the electrolytic plants are so far from the places where the oxygen is required that the cost of transport of the heavy cylinders is large.

The use of the oxyacetylene blowpipe flame for welding and for cutting through metal plates has recently extended so much as to lead to a greatly increased consumption of oxygen for this purpose. The readiness with which air is now reduced to the liquid state and from the liquid, both nitrogen and oxygen can be separated in a condition of approximate purity, are circumstances which again have led to a new position of affairs.

The liquefaction process can only be carried out on a relatively small scale, and consequently it is quite convenient to erect a number of plants in various places near where the oxygen is required, thus saving transport costs. The nitrogen obtained from liquid air can also be used for the manufacture of ammonia, but this method for the production of nitrogen is only used in places where electric power is cheap.

Before proceeding to describe the production of the gases from air it will be worth while to glance at the information now available as to the use of acetylene and oxygen for the purposes referred to. Acetylene is a gas familiar enough for lighting purposes and produced by the action of water on calcium carbide. The gas is supplied for the use of engineers dissolved in acetone and contained under pressure in steel bottles. When burnt acetylene gives out more heat than is represented by the carbon and hydrogen it contains, for it is an endothermic compound, that is to say, in the union of carbon with hydrogen in the production of acetylene, heat is absorbed.

Hence when the carbon and hydrogen are again separated the same amount of heat is evolved, and if this occurs while they are both uniting with oxygen a greater amount of heat is produced and a flame of higher temperature results.

By means of an appropriate blowpipe the two gases, acetylene and oxygen, delivered from their respective cylinders meet, and when ignited produce a pointed flame of which the temperature is considerably higher than that of a mixture of oxygen and hydrogen. A flame of this kind can be used for welding together iron surfaces of all kinds.

The use of the blowpipe, however, is still more wonderful in

the feats which it is now capable of performing in the direction of cutting thick sheets of metal. In this case the oxyacetylene flame is produced at the mouth of the blowpipe, and through the middle of this a pointed oxygen flame is directed on the surface of the iron or steel to be cut. The following quotation from Thorpe's Dictionary will serve as a sufficient illustration of the capacity of the method.

"A plate 12 inches thick of nickel chrome steel armour plate was cut through at the rate of 1 foot in $4\frac{1}{2}$ minutes with a consumption of 50 feet of oxygen per foot run."

With such an instrument at hand the older shearing, sawing, and boring methods of the engineering workshop have greatly decreased.

About four-fifths of the oxygen used in industry is required for the oxyacetylene blowpipe, the remainder being employed for medical purposes and for use where the supply of air is limited, as in submarines, mine rescue work, deep-sea diving and at high altitudes in flying and climbing. A small quantity of liquid oxygen is utilised, in the form of a mixture with carbon, as an explosive for blasting purposes.

The separation of liquid air into its chief constituents, nitrogen and oxygen, is based on the fact that under atmospheric pressure liquid nitrogen has a boiling-point, -196°C ., which is somewhat lower than that of oxygen, -183°C . From liquid air, therefore, nitrogen tends to evaporate off, leaving a liquid relatively richer in oxygen. The efficient separation of the oxygen and nitrogen is carried out by a process of fractional distillation or "rectification" invented by Linde, and improved by the famous French engineer Claude. In recent times the process has been slightly modified, although the principle remains unchanged, in order to separate the inert gases, especially the argon and neon which are used for filling half-watt lamps and glowing electric signs, respectively.

A diagrammatic representation of the apparatus is shown in Fig. 58, which will convey an idea of the nature of the process. The air to be treated is drawn through towers containing caustic soda in order to remove carbon dioxide and water vapour; in some cases a solution of caustic soda is used to absorb carbon dioxide and then the water vapour has to be frozen out by partial compression and cooling. The dry air is now compressed, and entering, as shown at the left-hand side of the figure, it

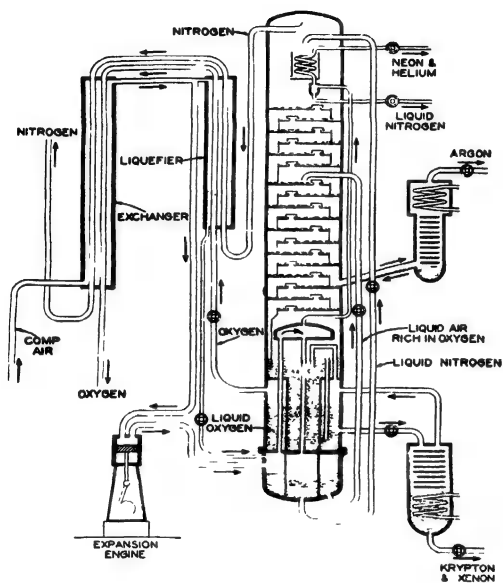


FIG 58 -DIAGRAMMATIC REPRESENTATION OF LIQUID AIR
RECTIFICATION PLANT

unites with oxygen forming solid copper oxides. The metal is readily regenerated by passing over it a stream of producer gas or any gas containing hydrogen or hydrocarbon vapours. A simple arrangement would therefore be to provide two cylindrical vessels filled with scrap copper maintained at a red heat, the one being supplied with air, while the other is fed with producer gas alternately. In actual practice at the present day nitrogen is obtained on the large scale by the use of carbon, in the form of coke, as the agent for withdrawing oxygen (see chapter XXVII). When air is passed over red-hot coke the resulting gas is a mixture of nitrogen and carbon monoxide, known technically as "producer gas." The carbon monoxide can be removed from the mixture by means of the reaction with steam, which has been already described.

Before closing this chapter mention may be made of the curious form of oxygen called "ozone"; whereas a molecule of ordinary oxygen contains two atoms, one of ozone contains three atoms of oxygen, and it is generally pictured as



The molecule tends to give up its third atom relatively easily and so it has strong oxidising properties.

Ozone is made by passing an electrical discharge through oxygen, and on the manufacturing scale a "silent" or "brush" discharge is used. The curious smell in the vicinity of electrical machinery is due to ozone. The gas is employed for sterilising water supplies in some places, and also for purifying air; it is also used as an oxidising agent in the preparation of synthetic vanillin, the odoriferous constituent of vanilla (p. 350).

Seaside air is often claimed to contain appreciable amounts of ozone, but this claim is unjustified, although relatively large quantities are present in the upper atmosphere, produced by the action of the ultra-violet rays from the sun on oxygen.

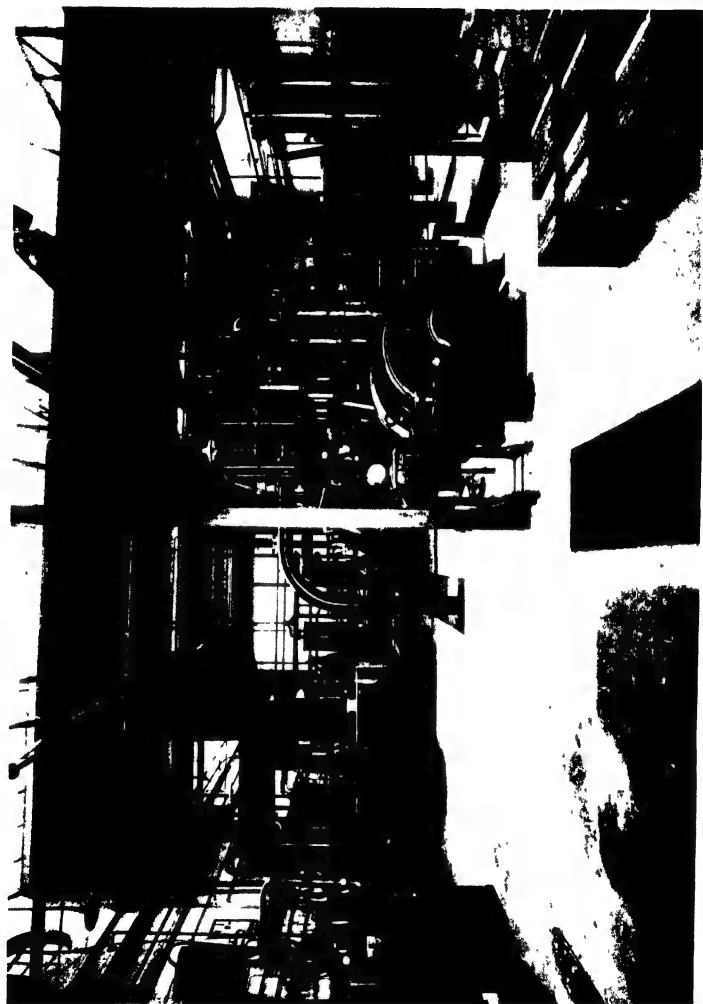


FIG. 59.—PLANT FOR THE PREPARATION AND RECTIFICATION OF LIQUID AIR

(By courtesy of the *British Oxygen Co. Ltd.*, Wembley)

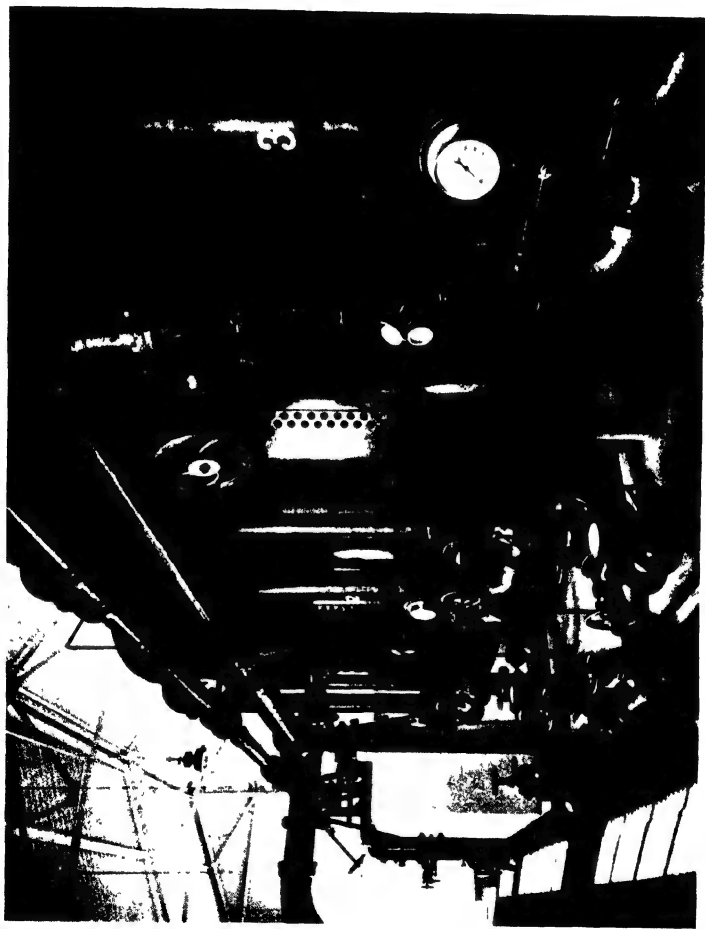


FIG 60 —LARGE-SCALE PLANT FOR SOFTENING OF WATER BY THE PERMUTIT PROCESS

CHAPTER XVI

WATER AND ITS PURIFICATION

THE provision of a sufficient safe and suitable supply of water has always been a subject of great public importance. But it is only within the memory of the present generation that the character of the impurities occurring in water used for drinking has been completely understood, and that due precautions have been taken in the selection and treatment of water to be supplied to towns for all purposes. Water as it falls from the skies in the form of rain, snow, and hail may be said to be, from the dietetic point of view, pure, that is, it contains in solution only a small quantity of the gases of the atmosphere. This is true of rain water falling in the country, but as is well known the rain in towns is always contaminated with soot and with acids, which are the result of burning coal containing sulphurous and arsenical minerals, to say nothing of acid impurities emitted from works where chemical operations, such as alkali, glass, or cement making are carried on. The water supplies are, however, always drawn from districts as remote as possible from influences of this kind, and are subject only to sources of contamination provided by nature, and dependent chiefly on the geological character of the strata through which the water rises or over which it flows. The impurities thus naturally introduced are of two kinds, namely, the inorganic and the organic. With regard to the former we have to remember that some saline or earthy matters are soluble in water without any addition or assistance, while others are dissolved only by water holding carbonic acid derived from the air.

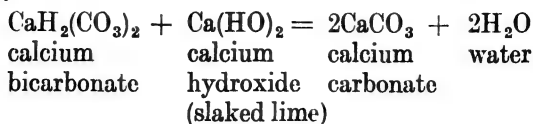
Thus while silica, alumina and minerals in which these substances predominate as constituents are practically insoluble in water, common salt, Epsom salt (magnesium sulphate), and gypsum (calcium sulphate) are more or less soluble in water, the two last giving rise to the quality commonly called *permanent* hardness in many natural waters. On the other hand, the carbonates of lime and magnesia are practically insoluble in pure water, but they are found as constituents of many natural waters derived from springs, lakes, and rivers, owing to the

presence of carbonic acid, by which they are taken up, forming unstable bicarbonates which are decomposed by boiling the water. The presence of these compounds gives rise to *temporary* hardness. Both these forms of hardness are the cause of some discomfort in washing and destroy soap with the formation of an insoluble curd, but, at least in moderate amount, they are certainly not injurious to health. They are, of course, mischievous when used in steam boilers, as they give rise to calcareous deposits and incrustations, known as "scale."

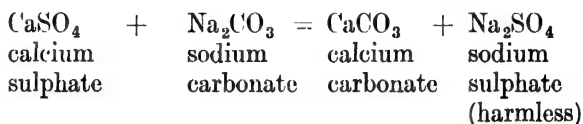
With regard to the organic substances found in water, much of this material is derived from the decay of vegetable matter, and it is commonly the cause of the various shades of green, yellow, or brown which are observable in the waters of streams and lakes. It is especially noticeable in water which has flowed or soaked through beds of peat, and may occur in water which, having passed only over hard silicious rocks, is comparatively free from saline or earthy impurity, and is therefore soft. Organic matter of this kind in moderate amount, as it occurs in the majority of waters supplied to communities, is not known to be definitely harmful as a constituent of drinking water. Down to comparatively recent times much ingenuity was expended in devising processes for estimating the amount of such substances in drinking water, but it is now recognised that the dangerous constituents in water are living organisms, and that the presence of much decomposing nitrogenous organic matter is significant chiefly as pointing to the probable contamination of water with animal excreta. The last may be derived from influx of sewage, surface drainage from land supplied with manure or other similar sources. The examination of water with the object of determining whether or not it is fit for drinking by human beings is therefore now dependent less on chemical analysis than on bacteriological processes, in which the number of pathogenic organisms in measured quantities of the water can be counted and their character determined.

The softening of hard waters containing carbonates of lime and magnesia can be effected by boiling the water, when the bicarbonates are decomposed and carbon dioxide escapes. This, however, is impracticable on a large scale, and in practice such water is dealt with by the addition of slaked lime in quantity which must be accurately estimated from a knowledge, obtained by analysis, of the composition of the water to be treated. The

chemical change which occurs is represented in the following equation :



A precipitate is formed which consists of the lime which has been added together with the lime previously held in solution, both in the form of carbonate. The water is, therefore, deprived of its hardness to this extent, and any hardness remaining is due to the presence of lime or magnesia in the form of chloride or sulphate. The latter can be removed by the addition of washing soda which consists of sodium carbonate, the chemical change occurring being written :



The lime-soda process of water softening is the one used on a large scale more than any other ; the resulting water is quite satisfactory for those industries, such as wool scouring, dyeing, and tanning, in which hard water is detrimental, and it can also be generally used to supply boilers for raising steam. Recent developments in high-pressure boilers have shown that water softened by the lime-soda process is not altogether satisfactory, since the little calcium sulphate left behind deposits in the boiler as the water evaporates forming a dense scale. By the addition of sodium phosphate, and sometimes a little alkali, in definitely calculated amounts to the softened water, calcium and magnesium phosphates and magnesium hydroxide tend to form in the boiler, but these separate as a sludge and not as a harmful scale. The process of water treatment for prevention of adherent scale formation in boilers is known as "conditioning," and is mainly due to the work of R. E. Hall in America.

An alternative method for softening water, which is of growing importance, makes use of the material known as "permutit." Although it is employed on a large scale in some places, it appears to be most suitable as affording a means of softening water in the home for domestic purposes, especially in limestone districts.

Permutit is an interesting case of the application of a mere laboratory product to practical purposes. The permutits are complex silicates, artificially produced, which have the property of exchanging their basic constituents when immersed in appropriate solutions. By melting together china clay (an aluminium silicate) and soda, a compound is formed which after being crushed and washed with water contains sodium, aluminium, and silicon oxides, and water, combined in proportions represented approximately by the formula $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.2\text{SiO}_2.6\text{H}_2\text{O}$. Its use is for the softening of waters which owe their "hardness" to the presence of lime and magnesia in the form not only of carbonate, but of sulphate, or chloride. If a permutit material is immersed in such water an exchange takes place between the sodium of the permutit and the calcium and magnesium of the water resulting in the formation of a solid compound containing the latter bases, while the water retains the harmless sodium carbonate, sulphate, and chloride. After a certain amount of the hard water has passed through the material the latter will naturally cease to act for the obvious reason that it is fully charged with lime or magnesia, and has nothing further to exchange for the earthy constituents of the water. The chemical law of mass action may then be put into operation, by shutting off the hard water and passing slowly a moderately strong solution of common salt in amount considerably in excess of the quantity of sodium required to restore the permutit to its original composition. Under these circumstances the calcium and magnesium pass away in the form of chlorides into the solution.

After the action is over the filter bed is washed free from the excess of salt and earthy chlorides, and is then ready for its renewed activity as water softener. In practice the softener consists of a cylindrical tank containing a bed of permutit of proper depth (according to the degree of hardness exhibited by the water) arranged between two layers of fine gravel. All the water supply required during the day passes through this bed and issues completely deprived of the hardening constituents. At night the water is turned off and the regenerative salt solution flows slowly through. In the morning the permutit is washed by passing a little water through it, and running the solution of chlorides to the drain. The ordinary water supply can then be resumed.

The same principle is applied when the purpose is to remove

iron which would be objectionable in manufacturing operations and which gives an unpleasant "inky" taste to water. In this case a manganese compound is prepared, and the regenerative liquid is a solution of permanganate.

The treatment of water intended for household purposes is generally carried out at municipal reservoirs, and may be divided into three main categories¹: (a) removal of suspended and colloidal substances, (b) reduction of hardness, and (c) destruction of harmful bacteria and other organisms.

The coarser matter suspended in water may be separated by simple sedimentation, but this does not remove the finely divided colloidal material frequently present in peaty and moorland water; the process generally used is to add a chemical coagulant, followed by sedimentation and then filtration through layers of sand and gravel. Aluminium sulphate, either alone or with a little lime or soda, is probably the chief coagulant in use; when added to water aluminium hydroxide is formed and in the course of precipitation drags down with it the suspended and colloidal matter. The action is to some extent, no doubt, due to the action on one another of oppositely charged colloidal particles (see chapter XIII). The use of aluminium sulphate is said not only to be advantageous for its precipitating effect, but also because it causes the deposition of a thin, gelatinous film on the grains of the filter which permits of more effective filtration. A modification of the aluminium sulphate process, which has been used at Darlington with great success and is also being tried out at Leicester, is known as "double coagulation"; aluminium sulphate and sodium aluminate are used which precipitate one another, forming aluminium hydroxide in a form which gives excellent flocculation and a good colour.

The softening of water at the water-works is not general, unless it has an exceptional degree of hardness; when it is necessary lime is generally used, so that the temporary hardness only is removed. In a very few cases a portion of the water is softened by the permutit method, which removes all the hardness, and this is then mixed with untreated water so as to give a water of medium hardness. When using the lime-softening process it is sometimes necessary to "carbonate" the water with carbon dioxide in order to prevent the precipitation of calcium carbonate

¹ For an excellent and authoritative account of water treatment by Dr. A. Parker, see *Chemistry and Industry*, 1935, p. 49.

in the pipes ; care has to be taken not to overdo this treatment, however, as the supply pipes then become liable to attack, thus introducing metals into the water and also causing corrosion.

Where lime is used for water softening it is often the practice to add a slight excess, for this has the effect of destroying living organisms ; a form of specially active carbon is added before filtration in order to improve the taste. This method has been successfully used at several water-works in Great Britain and the United States. On the continent of Europe, for example at Paris and Leningrad, ozonised air is employed for disinfection purposes ; it is said actually to improve the taste and appearance of the water. The process in most common use in England and America is to chlorinate the water, sometimes followed by ammonia to remove any unpleasantness of taste ; generally not more than 0.5 part of chlorine is necessary to a million parts of water.

Various other details require attention in the treatment of water, but sufficient has been said to indicate the main problems which have to be solved.

CHAPTER XVII

METALS AND SOME OF THEIR COMPOUNDS

THE term *metal* is still in use without the possibility of a strict definition. Seven metals were distinguished by the ancients and were in alchemical times associated in a fantastic manner with the names of the seven planets." Of these names Sol (gold), Luna (silver), Mercury (quicksilver), Venus (copper), Mars (iron), Jupiter (tin), Saturn (lead), only one, namely Mercury, has been retained in common use. The crude practices in the laboratories of the alchemists led to a few useful discoveries, among them probably the metal zinc, which was first mentioned by Paracelsus in the sixteenth century. In the latter half of the eighteenth century, at the time of Lavoisier, the number of recognised metals was seventeen. The popular idea at that time was, and is down to the present day, that a metal is a hard, shining, and heavy substance, which can be melted only in a hot fire. When therefore Davy in 1808 discovered potassium

and sodium, which are both lighter than water, some perplexity was caused by their anomalous qualities and for a time it was proposed to designate them merely *metalloids*. This term, however, with the authority of Berzelius, soon received a different application, and with further knowledge of the physical and chemical properties of these elements they were included in the category of metals. Somewhere about sixty substances are now called metals, but it would be difficult to secure complete unanimity among chemists as to whether particular elements should be included. There is, however, one test which would probably be accepted generally. In solution the ions of metals carry positive charges, so that they are always deposited at the cathode under the influence of an electric current; they are therefore spoken of as electro-positive elements, notwithstanding differences in other physical characters, such as density, fusibility, ductility, or brittleness.

Gold, which occurs in nature almost always in the native or metallic state, was probably the first known to primeval man. The others occur chiefly in the form of sulphides or oxides, and the common useful metals are for the most part obtained by reduction of their oxides. Even those which, like copper, lead, and zinc, are found in combination with sulphur are usually submitted to a preliminary process of roasting in contact with air, so that much of the sulphur is burnt off and an oxide of the metal remains which is subjected to further treatment.

The art of metallurgy has, however, undergone great developments and many modifications within recent years, owing especially to the introduction of the electric arc, which gives temperatures far above ordinary furnace heat, and the electric current by which the method of electrolysis can now be applied economically on a large scale. By the application of these modern agents some metals, calcium for example, are now obtained on a fairly large scale which a few years ago would have been found only in the form of small specimens, the product of a troublesome laboratory operation.

Space will not allow of the description of many of the processes which are now applied to the production of metals for industrial or practical purposes, but a few of the more important may be briefly mentioned.

SODIUM

In September, 1807, Humphry Davy began those experiments on the action of an electric current on caustic potash and caustic soda which resulted in the isolation of the two strange metals, potassium and sodium. On November 19th he gave his second Bakerian Lecture to the Royal Society in which he announced his discovery. Very shortly after this Gay Lussac and Thénard succeeded in obtaining potassium by heating caustic potash to redness in contact with iron turnings. These metals were afterwards made by distilling at a red heat a mixture of the carbonate with charcoal, and by this process they were made for upwards of fifty years. A modification of these methods was then introduced by Castner about 1887, but this has long been superseded by a process, also invented by Castner, which is identical in principle with that of Davy but adapted to operations on a large scale. Electric current is now obtainable at moderate expense, and sodium is made in large quantity by the electrolysis of caustic soda fused and kept at a temperature about 20°C . above its melting-point. Sodium is at the present time of much greater importance than potassium, as it is used in considerable quantities in the manufacture of various chemical compounds, among them indigo, several of the synthetic drugs, and the cyanides. These metals are not familiar to the public and cannot be handled safely by the inexperienced. Both potassium and sodium are silvery white, almost as soft as cheese and melt easily. They cannot be exposed unprotected to air, as they absorb oxygen and instantly become covered with a coating of oxide. Thrown into water they decompose it explosively with evolution of hydrogen gas and formation of a solution of the caustic alkali.

A few years ago sodium was consumed in rather large quantity in the manufacture of aluminium by heating it with the anhydrous chloride of that metal, but the extension of facilities for electrolytic methods, together with the dangers and uncertainties of the sodium process, led to its abandonment.

ALUMINIUM

Aluminium is probably the most abundant metallic element in the earth, as in the form of the oxide, alumina Al_2O_3 , it is

the chief constituent of many crystalline rocks and of all clays. The metal was first isolated in the form of powder by Wöhler, but it was not until about 1845 that it was obtained in a compact state and on a manufacturing scale by Deville. Aluminium is distinguished by its low density, which is only about 2·7 times that of water, and therefore about one-third the weight of iron. It is a good conductor of electricity, and although inferior to copper in this respect, it is rapidly replacing the latter for the long-distance transmission of electric power on account of its lightness and lower cost. It forms a very valuable alloy with copper, which is known as aluminium bronze. This was manufactured by the Cowles process before the difficulties in the reduction of pure aluminium had been overcome. To obtain the bronze a mixture of corundum (alumina) with charcoal and granulated copper is heated in an electric furnace. The carbon takes the oxygen of the alumina, while the copper unites with the aluminium and forms a fusible alloy to which larger quantities of copper can afterwards be added if required. This alloy has nearly the colour of gold, while it has great strength and elasticity.

The development of the motor transport and aircraft industries has resulted in the introduction of a number of aluminium alloys which are of great value because of their lightness and strength. The most important of these are "magnalium," containing magnesium, and "duralumin" which is aluminium with about 4 per cent of copper and a little magnesium; other alloys with copper, nickel and zinc are used in the construction of motor-car and aeroplane parts. Alloys of aluminium and silicon, together with small amounts of other substances, are finding application in shipbuilding, for after suitable heat treatment they are very strong and highly resistant to the corrosive action of sea water.

Aluminium has been manufactured for many years by submitting to electrolysis alumina (prepared bauxite) dissolved in fused cryolite, the double fluoride of aluminium and sodium. The operation is carried out in an iron pot lined with carbon which forms the cathode. The current is introduced by means of thick carbon rods forming the anode which dips into the mixture. The metal sinks to the bottom and is tapped off at intervals, while carbon monoxide gas escapes. In proportion as the metal is removed the supply of alumina is kept up by adding it to the molten mixture.

In the production of aluminium, as in so many other cases, the source of power is the energy of falling water, and factories have been established in connection with many of the great waterfalls of the world, such as Niagara, the Falls of the Rhine at Schaffhausen, and in our own country at Kinlochleven in Argyllshire, and in North Wales. The bauxite consumed in the production of the metal is chiefly from the South of France, but useful deposits exist in the southern United States, in Antrim, Northern Ireland, and elsewhere.

The remarkable increase in the use of aluminium during the past quarter of a century is shown by the following figures for the total world output of the metal.

WORLD'S OUTPUT OF ALUMINIUM

1909	30,000 tons.
1919	136,000 ,,
1924	171,000 ,,
1929	270,000 ,,
1934	171,000 ,,

The large fall in consumption in the past year or two is to be accounted for by the depression in world trade; the decrease in production occurred mainly in the United States, where 104,000 tons of aluminium were made in 1930, but less than 40,000 tons in 1934. The annual production of aluminium in Great Britain has been about 15,000 tons during recent years.

Aluminium is valuable not only for its lightness but on account of its peculiar behaviour toward acids and alkalis. It dissolves rapidly in diluted hydrochloric acid, but is very slowly attacked by sulphuric or nitric acids, and still less by vegetable acids. On the other hand it is dissolved by alkaline solutions with evolution of hydrogen. Hence aluminium is used in a variety of ways for making cooking utensils and in the storage of a great variety of foodstuffs, but it is important to remember that saucepans or pots of aluminium must not be cleaned with the assistance of soda.

In air aluminium soon becomes covered with a thin, almost invisible, film of oxide, which being firmly adherent protects the metal from further corrosion. This process of self-protection can be expedited and made more effective by the method of "anodic treatment"; the metal is made the positive pole in the electrolysis of a suitable solution, when oxidation occurs and the

resulting surface becomes immune to atmospheric corrosion. The anodic process is used for the treatment of aeroplane parts.

Aluminium melts below a red heat, and when heated in air it oxidises readily. A thin piece of aluminium foil in a bottleful of oxygen gas if touched with a red-hot wire disappears instantly with an extremely brilliant flash, leaving the white oxide behind. The combination of aluminium with oxygen is attended by the evolution of a larger amount of heat than is disengaged by the combustion of an equivalent quantity of any other metal. The consequence is that a mixture of aluminium powder with the oxide of another metal when heated at a single point enters into a violent chemical reaction, at the end of which the aluminium is converted into oxide while the other metal is found in the metallic state. The action is so violent in some cases, copper oxide for example, that a kind of explosion occurs and part of the metal is volatilised. A mixture of aluminium with various oxides has been turned to account for the isolation of some metals not previously known or obtainable with difficulty. The metal chromium, for example, is obtainable in this way, in a state of purity, also manganese, which had previously been known only in combination with carbon or with iron.

An ingenious application of this property of aluminium is found in the "thermit" process. A mixture of ferric oxide with aluminium powder is placed in a crucible with a removable bottom, and a fuse placed in the top of the mass being ignited; the whole mass becomes incandescent, and in a few minutes a layer of molten iron sinks to the bottom of the pot and can be run off into a mould. The method is applied to the repair of broken castings, or to joining the ends of tramway rails without removal. The mould being placed round the rail end receives the melted metal, and after solidification the excess of iron can be cut or ground away to the level of the rail. The temperature produced in the mixture is said to be about 3500°C. ; it is sufficiently high to melt every known metal.

The reaction in thermit being once started cannot be stopped, and this material has been found in many of the incendiary bombs used in the war.

STEEL

Man has been described as a tool-using animal, but the materials accessible in prehistoric times were very different from

those which are available now. The use of stone and bone certainly preceded that of any metal, and naturally the metals which were obtainable either in the native state, like gold and copper, or by very simple operations, would come into use before those which were more difficult to procure. The Stone Age therefore preceded the Bronze Age, and this came before the Iron Age, though doubtless these periods overlapped.

Modern metallurgy is the result of constant experiment and research. It has given the world modern steel, which means greater security on railway and steamship, greater capacity in foundry and forge, and consequently the monster ocean-going passenger ships as well as ships of war and big guns.

One of the difficulties which surround any attempt to give an account of some of these developments in a small space is to find a definition of steel. Everyone knows that it is a sort of iron but with qualities of its own. Pure elemental iron is a product which is extraordinarily difficult to obtain and is not found among commercial metals. The nearest approach to it is the finest malleable iron of which wire is made. This is distinguished by its fibrous texture, toughness, and capability of welding. Wrought-iron is fusible only at a white heat, but at any temperature above redness it is soft and can be hammered or drawn into any desired shape, and if at this temperature two pieces are hammered together they become completely united. This is, of course, the basis of the blacksmith's art.

The cast-iron from which wrought-iron is made is the product of the blast furnace. Iron ore, coal or coke, and limestone being heated together, the materials melt and settle to the bottom of the furnace in two liquid layers. The upper is slag, the lower is iron in union with 2 to 5 per cent of carbon, and small quantities of sulphur, phosphorus, and silicon. Iron of this kind is brittle, though hard and much more easily fusible than wrought-iron.

Steel is made by several processes, all of which have for their object the production of a carbide or mixture of carbides of iron containing an amount of carbon which may range from .1 per cent in mild steel up to about 2.0 per cent or a little more in hard tool steel. The presence of sulphur and phosphorus in steel is detrimental. Steel is in all varieties less brittle than cast-iron and has a greater tensile strength than wrought-iron. The milder varieties, that is those which contain the smallest percentage of carbon, can be forged and welded. The character

which formerly was considered distinctive of steel is its property of becoming hardened by quenching in water or oil when at a high temperature. The degree of hardness to be given can be regulated by the temperature to which it is heated and the rate at which it is cooled down. This is called *tempering* and is sometimes regulated by observing the colour of the film of oxide which is formed on the surface when the metal is heated. The blue colour of a watch-spring is familiar and is indicative of great elasticity: heated to redness and then plunged into cold water it becomes brittle. But during the last fifty years great advances have been accomplished in the knowledge of the internal structure of the metal by the aid, not only of chemical analysis, but the use of the microscope and a study of the peculiar phenomena which iron exhibits in changing temperatures. The introduction of electrical resistance thermometers, and of other pyrometers, now enables the manufacturer to test and regulate the temperature of his furnaces, a point of great importance which was beyond control only a few years ago. The constituents of steel have been the subject of very numerous researches, and even now authorities differ in some points of detail.

On heating a mass of steel to redness and then allowing it to cool slowly it is observed that the temperature does not drop regularly but at certain points the cooling seems to hesitate and proceed more slowly. There are three of these critical points or points of recalescence, namely, at about 825° , 735° , and 660° , observed in very mild steel. In hard steel the critical temperatures are both relatively and absolutely somewhat different, but similar phenomena are noticed. On gradually heating up a mass of steel the rise of temperature is retarded, showing an absorption of heat at about, but not exactly, the same points. These and other observations have led to the hypothesis that iron is capable of existing in two or more *allotropic* states, that is, states in which the atoms occupy different relative positions within the crystal of iron. These allotropic states differ in their capacity to dissolve carbon and in their magnetic properties.

In the harder steels carbon plays a very important part. It seems to be capable of dissolving in molten iron and on cooling it enters into chemical combination with the metal. One, and perhaps the most important compound formed, is *cementite*, to which is attributed the formula Fe_3C . The different varieties of steel when in the solid state may be supposed to be mixtures in various

proportions of this compound with one or other of the allotropic forms of the metal, or of a solidified solution of carbon in the metal. Many of the steels introduced into modern practice for special purposes contain other ingredients, some of which will now be described.

Manganese has been recognised as a necessary ingredient in steel ever since the introduction of the Bessemer and open-hearth processes for the manufacture of the metal. The amount present in ordinary steels does not usually exceed 1 per cent, but for special purposes manganese steels are made containing much larger quantities. The latter contain about 12 per cent of manganese and are characterised by exceptional strength and toughness, to which is added the remarkable property of becoming harder when subjected to heavy strain. Manganese steel is used for tram and rail crossings, for crushing machinery, dredger buckets, and generally where the conditions of use are exceptionally hard.

Nickel is a familiar white metal, which is about as difficult to melt as wrought-iron. Some forty years ago, when it began to be available on a large scale, various alloys of nickel with iron were tried and since that time have rapidly extended in use. Nickel added to iron has a toughening effect, and when added in proportions from 12 to 20 per cent it increases greatly both the tensile strength and elastic limit. Nickel steel has been largely used for armour plate. The magnetic properties of this alloy are remarkable; when about 25 per cent of nickel is present in steel it is almost non-magnetic unless exposed to a temperature of -40°C . After cooling to this low temperature it remains magnetisable at ordinary temperatures, but if heated to 600°C . it recovers its original non-magnetisable condition. This alloy has a high electrical resistance varying little with temperature, and so is used for making standard resistances. An alloy containing 36 per cent of nickel, called *Invar*, does not expand to any appreciable extent when heated, and a 45 per cent alloy, *Platinite*, with the same coefficient of expansion as glass is employed for sealing metal filaments into electric lamp and radio-valve bulbs. *Permalloy*, containing 80 per cent of nickel, has special magnetic properties which make it useful for telegraph cables and for use in radio-apparatus.

Chromium is a metal which was almost unknown till Moissan's introduction of the electric furnace. A ferro-chromium alloy

was formerly made in the blast-furnace, but chromium and other alloys for use in steel-making are now manufactured in the electric furnace. The metal can also be obtained by the thermit process already explained. Pure chromium is hard enough to scratch glass; it is somewhat similar to iron when polished but is not magnetic and is unaltered by moist air. It combines with carbon in several proportions, forming the carbide Cr_4C and at the higher temperature of the electric furnace the compound Cr_3C_2 (Moissan). Its hardening effect on steel appears to be closely connected with the amount of carbon present.

Steels containing small amounts of chromium have been in use for many years, but in the past two decades an entirely new series of chromium steels has attained great importance. The presence of about 12 per cent of chromium gives the ordinary type of stainless steel used extensively for cutlery, whereas steel with 18 per cent of chromium and 8 per cent of nickel is brighter and has a greater resistance to corrosion; the latter alloy is particularly suitable for use in the chemical industry. A still higher proportion of chromium, together with some nickel, gives alloys having heat-resisting properties. The property of resisting attack conferred on steel by chromium is attributed to the fact that the latter metal is readily oxidised, forming a very thin, invisible oxide film adhering so strongly to the surface of the steel that all further attack is inhibited. Solutions containing chlorides tend to disintegrate the oxide film and so corrode the stainless steels.

Tungsten is a very infusible metal found in the form of the mineral wolfram which is a tungstate containing the oxide WO_3 . This compound can be reduced to the metallic state by heating with coke in the presence of cast-iron. The product is known as ferro-tungsten, and is used as an alloy in steel for the production of so-called "self-hardening" steels. It is associated with manganese in the once well-known Mushet steel, although the use of chromium instead of manganese gives a better steel for heavy cutting work and Mushet steel is now obsolete. These steels are incapable of being made soft by any known method and are used particularly for high-speed cutting, in which the tool gets extremely hot but does not lose its edge.

An alloy of tungsten and carbon, with a few per cent of cobalt, known as *carbology* or *widia* yields the hardest cutting edge for work in steel; until its discovery in 1926 it was impossible to

machine manganese steel, but with the aid of tools tipped with the new alloy this can now be done.

Molybdenum and *vanadium* are frequently added in small amounts, together with other elements, to increase the strength of steel; the former is often used instead of tungsten. Vanadium has a curious history, for the substance which during forty years had passed as the metal itself was shown by Roscoe to be a compound of that substance with nitrogen. Vanadium though not rare is far from abundant, and the cost will necessarily have the effect of limiting its application in steel-making to special purposes. Fortunately the addition of very small quantities of vanadium is sufficient to modify the properties of steel substantially. The addition of 0.6 per cent of vanadium to a pure iron and carbon steel (containing 1.1 per cent of carbon) raises its tensile strength from about 30 tons to 85 tons per square inch.

Titaniferous iron ores exist in immense quantities in Sweden and in the form of sands in the United States, Canada, and New Zealand. In the blast furnace only a portion of the titanic oxide, TiO_2 , is reduced and passes into the iron. There has been difficulty in introducing titanium into steel, but the presence of a small quantity is said to assist in the production of a sound ingot. It has a tendency to combine with nitrogen and may in this way prevent the formation of blowholes.

NICKEL

This metal is very familiar in the form of nickel plating, and has long been used as an ingredient in the white alloy with copper of which electro-plated dishes, spoons, forks, and other table furniture are made. But the very interesting and remarkable process by which a large proportion of the pure metal is made is based on a modern discovery which dates back no further than 1890. In that year a paper in the *Transactions of the Chemical Society*, by the late Dr. Ludwig Mond, associated with Dr. C. Langer and Dr. F. Quincke, announced the discovery of the fact that when metallic nickel, especially in a finely divided state, is heated gently in a stream of carbon monoxide gas a volatile compound is formed which consists of the metal in union with carbon monoxide. The escaping gas burns with a brightly luminous flame, and when heated to a temperature of

about 180° it is resolved completely into the gas and the metal, the latter being deposited in the form of a lustrous mirror-like solid. When the mixture of gases is passed through a glass tube surrounded by a freezing mixture of ice and salt the compound is condensed to a colourless, mobile liquid, a little heavier than water, and boiling at 43° C. The liquid has the formula $\text{Ni}(\text{CO})_4$; it is not acted on by acids or alkalis. It precipitates copper and silver from ammoniacal solutions of the chlorides of those metals, but in general it behaves as a neutral compound.

It is easy to see how these observations may be turned to account in the extraction of nickel from the mixed ores from which so much of this metal has been obtained. The ores which contain a number of metals, iron, copper, cobalt, nickel, etc., in the form of sulphide and arsenide are first roasted, by which the greater part of the sulphur and arsenic is expelled and the metals converted into oxides. These are then heated moderately in a stream of producer gas whereby the oxides are reduced to the metallic state, and the temperature being duly regulated, the carbon monoxide in the gas unites with the metallic nickel and carries it off, while the other metals which form no volatile compound are left behind in the residue. The nickel is recovered by causing the mixed gases to pass through a heated pipe before being returned to the furnace to play the same part over again. It is to the discovery of this process, by means of which the largest proportion of the world's production of nickel is isolated, that the greatly increased application of the metal is to be attributed.

Very large quantities of nickel are also made from the mineral called garnierite, which consists of a hydrated silicate of nickel and magnesium and is found in New Caledonia. This mineral is practically free from other metals, and the nickel is obtained from it by a furnace process which consists in first converting the metal into sulphide, and then reducing it by a series of operations similar in principle to those by which copper is obtained from its sulphide ores.

Nickel is a white metal a little heavier than iron but having the advantage of practical permanency in the air whether dry or moist. It is somewhat magnetic.

The use of nickel in connection with steel and in a variety of alloys with iron has been already mentioned; in addition a number of other alloys are important. Nickel-copper alloys are

particularly worth mention ; they are easily worked and have a high resistance to corrosion. In the form of *silveroid* and *monel metal* these alloys are now being used for shop fronts, doors, kitchen sinks, and other domestic purposes. Alloys of nickel with copper and zinc (*nickel silver*), with copper and tin (*nickel bronze*), with copper and aluminium, and with gold (*white gold*) are extensively used.

Nickel is also employed in the pure state for various industrial purposes, for nickel electro-plating, and as a catalyst, prepared from the sulphate, in hydrogenation processes.

LAMP FILAMENTS

Great progress has been made in connection with illumination to which the study of metals has contributed. Up to the time of the great Exhibition in 1851, and for many years later, the interiors of houses had been lighted by candles, and the snuffer tray was a necessary article of daily domestic use. The streets of London and of most towns were at the same time provided with lamps for coal gas which was burnt at flat flame burners, giving a degree of illumination which would be regarded as intolerable at the present time.

The discovery of large quantities of petroleum in Pennsylvania about 1860 provided a new and cheap source of light, and there was soon great activity among the lamp-makers. The use of gas as an internal illuminant for houses was still, previously to 1860, though common, far from universal.

With the development of various forms of magneto-machine and ultimately of the dynamo which occupied many years, the electric arc gradually became available for use in lighthouses and here and there for large spaces such as the Thames embankment and in a few large workshops. But the arc was never suitable for domestic use, and it was only when the incandescent lamp, with a carbon filament enclosed in a vacuous glass globe, was invented that electric light became a practical source of light for internal illumination. Several conditions were necessary ; first electric current was wanted at a moderate price, and next the means of producing a high vacuum pretty easily was also indispensable, especially as the filaments to be made luminous by the current were all at that time made of carbon. Sprengel's mercury pump, invented in 1864, provided the means of getting

a vacuum, but there were great difficulties about the production of threads of carbon. The late Sir Joseph Wilson Swan after experiments made so long ago as 1860 exhibited the first electric glow lamp in February, 1879, at a meeting of the Newcastle Chemical Society, and in November, 1880, gave a demonstration at the Institution of Electrical Engineers in London. His carbon filaments were first made by heating parchmented thread, and later by squirting collodion through a die. These were exhibited at the Inventions Exhibition in 1885.¹ Mr. T. A. Edison, the well-known American inventor, had in the meantime begun working on the subject, but rival claims disappeared under a prudent and amicable arrangement, and in the end the Edi-Swan lamp became familiar to everyone.

In more recent years, however, the filament to be heated, and so made luminous by the current, is more usually made of some metal of low conducting power. Platinum was the first in which the phenomenon of luminosity produced by the current was studied, but platinum, though its melting-point is high, is too fusible for use in the lamp. It has one property which has made it useful in the lamps and that is its low coefficient of expansion. As it expands and contracts with change of temperature to nearly the same extent as glass a wire of this metal can be melted into glass and on cooling the glass does no crack. Hence platinum may be used for making the connections between the fittings outside the lamp and the filament which gives the light within, but actually the nickel-iron alloy, platinite (p. 264), is generally used.

Many metals and alloys have been tried for the production of lamp filaments, the object being to obtain the maximum of light with the minimum expenditure of current. The first of these was made from osmium, but owing to the high cost of this metal and its fragility it did not meet with much success. In 1905 the use of tantalum in incandescent lamps was first proposed. This metal was discovered by Ekeberg in 1803 in two Swedish minerals, tantalite and yttero-tantalite, but until the electric furnace provided the high temperature necessary it had not been melted and was known only in the form of a black powder. Tantalum is a white metal with a specific gravity 16.8. It melts at a very high temperature, said to be 2798° C., and it

¹ A collection of apparatus used in Swan's early experiments is now exhibited in the Science Museum, South Kensington.

is for this reason that it was tried as a lamp filament. The use of alternating current made the wire brittle, however, and so the tantalum lamp did not attain great success.

Tungsten, with a melting-point even higher than that of tantalum, has proved to be most satisfactory for filaments in electric lamps and in radio valves ; for a long time its use was hindered by the difficulty of drawing it into wires, but a satisfactory method is now available. Tungstic oxide is reduced in a current of hydrogen giving a powder of metallic tungsten ; this is heated in an electric furnace, when the particles of metal adhere to one another to form a homogeneous but brittle bar. As a result of special heat treatment the metal is made malleable, and by alternate heating and hammering it is reduced to a long rod of about a millimetre thickness. This is then drawn whilst hot through a series of diamond dies ; each die reduces the thickness by a minute amount so that some forty or fifty are necessary to give an ordinary filament.

In modern lamps and valves molybdenum wires are used to support the tungsten filament.

PYROPHORIC ALLOYS

A return to the flint and steel with the tinder-box of our forefathers is improbable for everyday purposes, but the discovery of the property exhibited by cerium and some of the other metals of the same group of so-called rare earths (see chapter VI) has led to the invention of contrivances for striking fire which are now in common use.

The metal cerium, obtained by the electrolysis of its chloride or fluoride, resembles iron in appearance but is far more fusible as it melts at 623°C . It is also much more easily oxidisable, decomposing water slowly, and in moist air it soon becomes coated with a film of oxide. The metal burns when ignited even more brightly than magnesium, and when scratched with a steel edge or struck by a flint it emits brilliant sparks. This property has been turned to account in the production of gas lighters and cigarette lighters for the pocket. Pure cerium is, however, less suitable for this purpose than certain mixtures of the cerium metals with iron, which are harder and yield sparks much more readily.

Cerium salts form a considerable by-product in the extraction

of thorium for the manufacture of incandescent gas mantles (chapter XVIII), and the production of the so-called "flints" for automatic lighters is one outlet for this material. The cerium residues, in the form of chlorides, are fused and an electric current passed through, resulting in the deposition of a mixture of rare-earth metals known as "*mischmetall*," consisting mainly of cerium and lanthanum. This substance is melted with about one-third of iron, and the alloy cast into moulds to form the familiar rods.

COMPOUNDS OF METALS

It is scarcely necessary to say that the metals by combining with other elements produce a very large number of definite compounds. Some of them yield several distinct oxides by combination with different proportions of oxygen, and all metals produce salts, which may be said to be their characteristic compounds. Many of these, such as common salt, alum, green and blue vitriol, have been known from the most ancient times, but scores of new compounds of this kind are added to the list every year, as the result of operations in the course of chemical research or manufacture. Many metallic compounds are applied to useful purposes as chemical agents, in medical practice, or as pigments and otherwise. These, however, are the commonplaces of practical chemistry, and information concerning them is stored up in the larger textbooks and dictionaries of chemistry, and to these sources of information the reader who desires it must be referred.

A few words may be added here as to the artificial production of certain gems. This is the outcome of conveniences for the production of high temperatures, such as the oxyhydrogen flame and the electric furnace. It need scarcely be repeated that the diamond is a form of carbon and that the diamonds produced by Moissan's process (p. 64) so far are minute and are of no use as gems. The ornamental stones, often very beautiful, which are sold in imitation of diamonds are merely artificial silicates containing lead and other heavy metals. Other stones such as emerald, garnet, topaz, etc., are also imitated by glasses, but the most interesting of artificial stones are the ruby and the sapphire which are now produced commercially by the fusion of pure alumina, of which both are essentially composed. The artificial stones are not merely imitations, they are identical in hardness,

density and crystalline form with the natural gems. They can, however, be distinguished by the difference in the fluorescence they show when exposed to cathode rays. Ruby owes its colour to the presence of a minute quantity of chromium in a peculiar condition of oxidation, and according to the late Professor Frémy, sapphire contains the same element in a different state. In this case the blue colour is more like that which is imparted to fused substances by cobalt, though it has also been attributed to titanium. As to the rest of the precious stones the cause of the characteristic colours is not in all cases known. Thus the emerald and aquamarine are varieties of beryl which probably owe their green colour to the presence of iron in the ferrous state; that of emerald has, however, been attributed to chromium and even to organic matter. Iron in the ferric state and manganese are capable of producing various shades of yellow, red, or purple, according to the states of combination in which they occur, and to one or both of them together the amethyst, the garnet, and other stones probably owe their colour.

CHAPTER XVIII

LUMINOSITY OF FLAMES

THE INCANDESCENT MANTLE INDUSTRY

EVERYONE is familiar with the facts that the flame of a candle, an oil lamp, or ordinary coal-gas is more or less luminous, while burning hydrogen, spirit of wine, or gas mixed with air, as in the Bunsen burner, gives so little light that such a flame in broad daylight is scarcely perceptible and in sunlight is actually invisible. What is the cause of this difference? The attempts to answer this question have occupied experimental chemists for upwards of a hundred years, and though many hypotheses have been put forward it cannot be said even now that the complete solution of the problem has been discovered.

Sir Humphry Davy was the first to enquire systematically into the source of light in flame, and in 1816 he put forward the opinion that the production and ignition of *solid* particles within the flame itself is the cause of the light. With regard to the luminosity of coal-gas he attributed the effect to the decom-

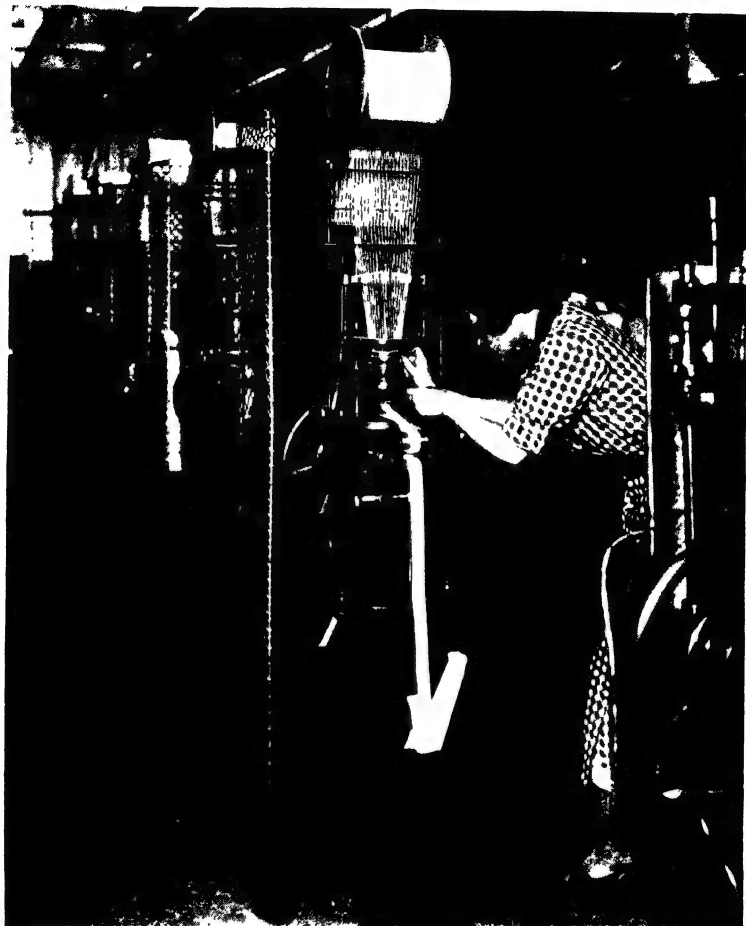


FIG. 61.—KNITTING MANTLE HOSE

(By courtesy of Lighting Trades Ltd. and the Welsbach Light Co., Ltd.)

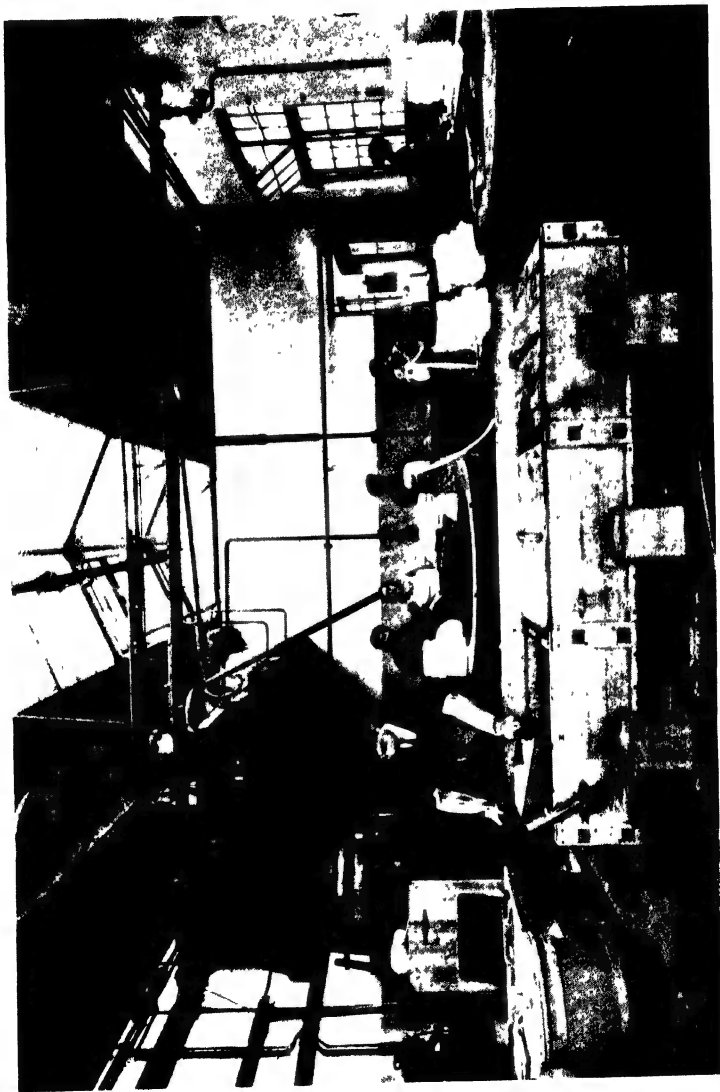


FIG 62 — WASHING MANTLE HOSE BEFORE IMPREGNATION
(By courtesy of Messrs. Falk, Stadelmann & Co. Ltd.)

position of a part of the gas towards the interior of the flame, where the air is in smallest quantity, and the deposition of solid charcoal, which by its ignition and afterwards by its combustion increased to a high degree the intensity of the light. "A few experiments," he says, "convinced me that this was the true solution of the problem." Nearly half a century later, however, Frankland drew attention to the fact that flames may be produced which are brilliantly luminous but contain no solid matter, and further that a gas like hydrogen, which burns under ordinary conditions without emission of light, may be made to give out light if burned under increased pressure. It appeared, therefore, that the light of a flame might be due only to the presence in it of dense gases or vapours.

Notwithstanding these results it appears certain for reasons which cannot be discussed that ordinary hydrocarbon flames, such as those of coal-gas, do contain solid particles, and a reason has to be sought for the deposition of carbon from the burning gas. The hypothesis brought forward a few years ago by the late Professor Vivian Lewes, which involved the production and immediate decomposition of acetylene within such flames, was at one time much discussed, but seems to be no longer tenable, and we are still waiting for "the true solution of the problem" which Davy thought he had got hold of over a hundred years ago.

That the introduction of solid matter into a non-luminous flame causes the emission of light is a matter of common knowledge, and Davy himself showed that it is of no consequence whether the solid is combustible or not, for he showed that not only the dust of charcoal but fine powder of silica or magnesia thrown into a flame produces light. From the time when coal-gas in the earliest years of last century became a common source of light, efforts have continuously been made to increase its illuminating power, first by the improvements in the jets or burners at which the gas was burned, later by the introduction of gases or vapours rich in heavy carbonaceous compounds.

Berzelius in 1829 noticed that thoria, zirconia and other of the rare earths in a non-luminous flame give out a very brilliant light, and similar observations were made later by Bunsen and other chemists. Lime is one of the substances which when strongly heated gives a bright light, but the temperature required in this case to give a satisfactory effect is higher than

that of an ordinary flame. The well-known limelight, in fact, requires the use of oxygen with the gas to produce the necessary temperature. It was only toward the latter end of last century that serious attempts began to be made to utilise the earlier observations of Berzelius and Bunsen on the peculiar incandescence produced by several of the rare earths. It is unnecessary to trace the various attempts to utilise the incandescence of magnesia, zirconia, and other substances, for the discoveries made by Dr. Carl Auer,¹ as a consequence of his studies of the rare earths begun about 1885, require all the space which can be spared for this subject. The "mantle," which is familiar in almost every household where gas is the illuminant, consists of a mixture of thorium oxide with about 1 per cent of cerium oxide. The use of this mixture was the result of a long series of trials, and was protected by patent in 1893. Since this discovery minerals which contain thorium have become very important and valuable.

At one time they were known chiefly as of Swedish origin and were even called the Swedish earths. But the immense quantities now required are supplied from *monazite* sands found in extensive deposits in N. and S. Carolina, in Southern India, and especially on the coast of Brazil. Other important minerals are *thorianite*, an oxide very rich in thorium, found in Ceylon, and *thorite*, a silicate which occurs in various localities in Scandinavia. *Monazite*, which is essentially a phosphate of cerium containing relatively small quantities of thorium, approximately 5 per cent, is the chief material now used in connection with the mantle industry.

Its composition is, however, very complicated, and the extraction of the small percentage of thorium present is a matter of difficulty.

In dealing with Brazilian monazite sand the first operations are mechanical, and advantage is taken of the high specific gravity of the mineral (about five times heavier than water) to remove by streams of water much of the lighter material. Electromagnets are also used for extracting ferruginous particles, and a concentrated material is ultimately arrived at which retains only 2 or 3 per cent of impurity. The mineral is then treated with sulphuric acid for the extraction of the earths.

Here, however, we may halt, for an exposition of the details

¹ Later known as Baron Auer von Welsbach.



FIG 63 —IMPREGNATING MANTLE HOSE
(By courtesy of Lighting Trades Ltd. and the Welsbach Light Co., Ltd.)



FIG 64—SEWING AND SHAPING ARTIFICIAL SILK MANTLES

(By courtesy of Messrs. Falk, Stadelmann & Co., Ltd.)

of the process to be followed would be extremely tedious to the general reader, and would be useless to the technical reader unless furnished with minute particulars. For those who desire to pursue the subject there exists several recent works on the rare-earth elements which contain full information.

The earliest "incandescent mantles" were made from cotton fibre, but these were liable to shrink and suffer contortion whereby they were often withdrawn from the flame and so produced less light. The luminosity was also reduced in the course of use by the presence of small quantities of mineral impurities left after the burning of the vegetable fibre. Ramie, obtained from the plant *Rhea Elastica*, is superior to cotton as a basis for making mantles, and has become the most popular fibre for the purpose. Artificial silk is said to be still better, as it is practically free from mineral matter, and it is used for manufacturing the flexible, non-fragile mantles.

The process of mantle-making consists in first knitting from a fine ramie, cotton, or artificial silk thread, a continuous cylindrical hose on a rotary knitting machine, the length of the stitch and the tension of the thread being regulated according to the width and depth of mantle required. The hose is then made up into loose bundles for washing in order to remove silicious and calcareous matter present in the fibre.

The washing process varies in different factories, but its object is, first of all, the removal of the grease and silica by digestion of the stocking with a weak solution of caustic alkali, followed by thorough rinsing in distilled water. The excess of alkali and the lime are afterwards removed by steeping the knitted fabric in a weak solution—1 to 2 per cent—of hydrochloric acid or acetic acid. The acid is then removed by agitation of the fabric in distilled water, and, if the hose is required to be kept any length of time, this is followed by a bath of dilute ammonia. The stocking is dried at a low temperature by hanging over poles or drawing continuously through a hot chamber through which a current of hot air is blown. It is then cut up, usually on a machine which cuts the fabric into pieces of equal length and width, stacks them, and automatically counts them as cut. In some cases the fabric is not cut into lengths until after the impregnation process, which it undergoes next, and just prior to "burning off."

We must now treat the upright and inverted mantles separately.

The heads of the upright mantles require to be reinforced by stitching on to them a piece of cotton or ramie tulle, with the object of strengthening the head and keeping it to a uniform size. They are then dipped in the previously prepared strong solution of thorium nitrate with about 1 per cent of cerium nitrate and .5 to 1 per cent of hardening materials, such as aluminium, zirconium, beryllium, or calcium nitrate, and put through gutta-percha rollers, carefully adjusted to leave exactly the right quantity of thorium nitrate in the mantle. The stocking is then dried upon glass forms, and when dry the head is reinforced with a further supply of solution containing a higher proportion of the hardening materials. The mantles are again dried and then sewn with asbestos thread to form the head.

The next operation is that of burning off the organic matter of the mantles, and at the same time decomposing the nitrates with which they are impregnated. The stocking is first shaped over a wooden form and hung up by means of an iron hook, fired, and allowed to burn until nothing but the white ash of thorium and cerium oxides remains. This ash is now in a loose condition and is extremely fragile. With the help of a burner supplied with either gas or air at a pressure of from 5 to 15 lbs. per square inch, the mass of oxides is blown out to its correct shape, and, by an up and down movement of the burner inside the mantle, the latter is brought to its final state of hardness, the change being due to the partial "fritting" of the more fusible oxides in the mantle. In this state the mantle is in the same resistant condition as when it is finally used upon the burners, but for purposes of transport it is coated with a varnish consisting of nitro-cellulose and various oils, to modify the too rapid character of the combustion of the nitro-cellulose. The mantles are dipped, usually from 40-60 at a time, in this "collodion" solution, allowed to drain and dried in ovens heated by high pressure steam. They are then able to withstand the handling necessary for examination, cutting to length, and testing to size and for minute holes, due to traces of silica adhering to the original yarn.

In the case of the inverted mantles, these are impregnated after being cut into suitable lengths and are dried upon glass forms. They are then mounted upon rings with an asbestos thread, and the other end of the stocking is drawn together by hand or by machines, and darned with a thread impregnated with the same solution as that in the body of the mantle. The



FIG 05 MANTLE TYING

(By courtesy of Lighting Trades Ltd and the Welsbach Light Co., Ltd)



FIG. 66 —MANTLE FINISHING.

(By courtesy of Lighting Trades Ltd and the Welsbach Light Co., Ltd.)

fixing fluid is then sprayed on to that portion of the mantle which is adjacent to the magnesia ring in order to give it extra strength at this point. It is then ready for burning, which is conducted in the same way as with the upright mantles.

The inverted mantles are dipped in collodion, dried, tested to see that they are perfect and that they fit the burners properly, and packed into units and dozens for sale.

When making incandescent mantles from artificial silk fibres the process is modified somewhat : in the first place the elaborate washing of the fabric is unnecessary since it is almost entirely free from grease and mineral matter. Secondly, after the impregnating stage, which is carried out in a similar manner to that employed for ramie fibre, the mantles cannot be burnt off directly, for if this were done the nitrates would make the skeleton of the mantle very fragile. The nitrates must, therefore, be converted into other compounds of the thorium, cerium, etc., present ; this is accomplished by first drying the mantle and then immersing it in a solution of ammonia or of hydrogen peroxide. The subsequent treatment is then similar to that already described : the fabric, now impregnated with insoluble hydroxides or oxides, is washed, dried, cut, burned off, and shaped in the usual manner.

In modern factories a certain proportion, from 1 to 2 per cent, of the mantles are tested for resistance to shock by being burnt off and mounted on the burners illustrated with the shocking machines. At the foot of these burners is fixed a bar at right angles to the burner stem, and the machine is arranged so that a little stamp battery, having weights of 2 to 5 oz. on each side, can be run at different speeds upon this bar, and submit the mantle to the same sort of vibration as it might experience when mounted in a lamp-post adjacent to a road gully over which a heavy lorry is passing.

The rings for support of the inverted mantles are composed of a mixture of china clay and silica with a small proportion of magnesia. For rings which have to resist a very high temperature, as when high-pressure gas is used, from 10 to 40 per cent of carborundum is added. The mixture of powders, moistened with a special oil to make it cohere when pressed, is squeezed into a metal die, made of three or four pieces which move together in a machine contrived for the purpose. After pressing into shape the rings are weathered for a period from two days to a

week, and are then scraped to remove rough edges and give them their finished shape. They are then packed in fire-clay boxes, called saggars, which are stacked together in a pottery furnace or kiln where they are baked. The baking which requires slow heating up and cooling down occupies about two days. The rings are then examined, brushed to remove dust, and the perfect ones packed in layers to be sent to the mantle factories.

The world production of mantles is approximately 300 million per annum, the individual amounts made in the chief producing countries being roughly as follows :

Germany	90,000,000
United States.	80,000,000
Great Britain	60,000,000
France	20,000,000

About one ton of pure thorium nitrate is required for each million mantles, and so about 300 tons of this substance, worth about £2,000,000, are used annually.

Such figures supply occasion for remarking on the rivalry which has existed for many years between the several systems of lighting our streets and houses. When the incandescent electric lighting began to make way, the gas industry appeared almost doomed to extinction so far as illumination was concerned, and great efforts were made to increase the candle-power of the gas manufactured, and to improve the burners in use. Then came the Welsbach mantle, and all seemed well for a time. But a new difficulty arose when the supply of the Swedish earths began to be exhausted, and the earliest Welsbach Company came to an end. The search for thorium-bearing minerals in other parts of the world, however, was soon rewarded by the discovery of inexhaustible deposits of monazite sands on the other side of the Atlantic. These deposits are now the basis of the vast industry which has been described in this chapter. Simultaneously the character of the coal-gas produced at the gas works has gradually undergone considerable modification, for, with the assistance to the illuminating power afforded by the mantle, it is no longer necessary to furnish gas of the relatively high candle-power formerly demanded. The effect of this is that a larger quantity of gas can be extracted from a ton of coal than was formerly possible when an illuminating power equal to 16 candles per 5 cubic feet was required. In fact whereas less



FIG. 67 SHAPING AND BURNING MANTLES
(By courtesy of Messrs. Falk, Stadelmann & Co., Ltd.)

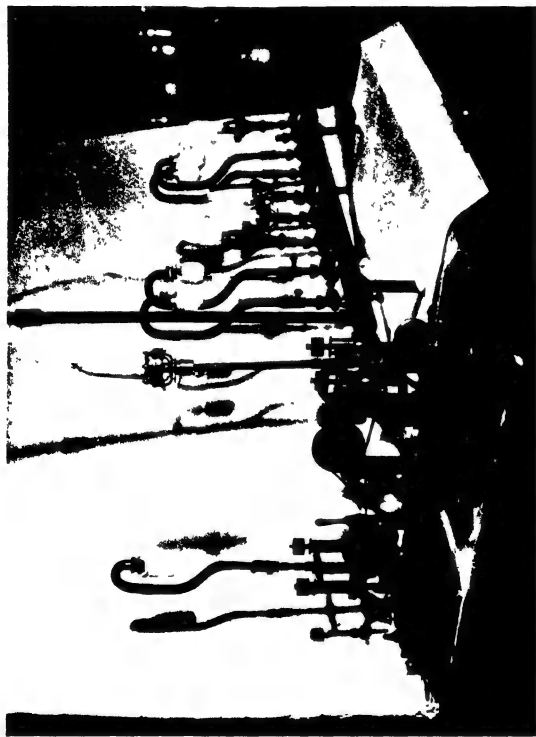


FIG 68 —TESTING MANTLES BY MEANS OF STAMP BATTERIES

than 10,000 cubic feet of gas were obtained per ton of coal heated, the yield is now over 14,000 cubic feet. A cheap gas produced by the addition of water gas charged with vapours from petroleum (see "Petrol") also helps to reduce the cost. The testing of gas, for statutory purposes, now relates to its power as a source of heat and it is well known that gas is now sold by the "therm," which is a measure of heating efficiency.

Simultaneously with the improvement in gas illumination there has been progress in electric lighting, particularly the invention of the gas-filled "half-watt" lamp. In spite of this gas is holding its own, especially for street lighting, mainly due to improvements in the design of burners, by pre-heating the gas before burning, by the use of a number of small inverted mantles, and by the aid of reflectors. The following figures referring to street lighting in South London show the change which has occurred during the present century; in the year 1899 flat flame burners were general, but in 1902 upright incandescent mantles were introduced.

STREET LIGHTING IN SOUTH LONDON

Year.	No. of gas lamps.	Equivalent candle power.	Candle-hours per cu. ft. of gas.
1899	20,998	280,000	2.5
1902	21,800	1,190,000	14
1913	24,713	1,700,000	19
1930	24,529	2,290,000	25

The steady improvement in efficiency of the lamps is evident.

The mantle industry is only one of many examples which could be quoted of the ultimate practical application of the results of purely scientific research to common industrial purposes. A generation ago the salts of thorium and cerium, lanthanum and didymium, and the rest were interesting only to a few enthusiasts. The place of these elements was and continues to be among the problems perplexing to the scientific chemist, and they were only known to exist in a few comparatively scarce minerals found chiefly in Scandinavia, and all this was implied in the name which for so long a time they bore, namely, "the rare earths." Now these elements are known to be widely diffused and available in any required amount from mineral deposits which are actually handled to the extent of thousands of tons annually, although the name rare earth-elements is still used.

CHAPTER XIX

PETROL

LESS than thirty years ago the arrival of any sort of motor vehicle in a country place would have been sufficient to bring together a crowd of wondering folk, and not many years ago any street in London exhibited a collection of omnibuses, carriages, wagons, carts and other vehicles of which the majority were drawn by horses. The proportion of motor to horse-drawn carriages is now so much changed that there is a prospect that in a few years the horse as an agent of traction will become as great a curiosity as the motor was a generation ago.

This state of things has been brought about by the development of various forms of internal combustion engines, of which the gas-engine, introduced about 1876, is one form from which engines capable of working with the vapour of a volatile liquid have been developed. The perfection of engines of this type applicable to every kind of moving vehicle, including the aeroplane, has occupied the attention of the engineer for many years past, and the supply of suitable "spirit" for the motor is a business of importance second only to that of the supply of coal. Motor spirit is derived almost entirely from the lighter and more volatile portions of natural petroleum, which is now known to exist in vast quantities in the earth, and distributed very widely. There are, in fact, few countries in which it is not found in greater or less amount. The value of petroleum as a fuel has become greatly enhanced of late years, since it has become more commonly used as a substitute for coal in locomotives, and in ships, especially in ships of war. Apart, however, from its utility as a fuel petroleum has been the subject of innumerable researches in the hands of the chemist, and in addition to the use of the constituent hydrocarbons actually existent in it which receive a great variety of applications, there is some reason for believing that certain of them may hereafter be transformed by chemical processes so as to yield valuable compounds of a totally different nature.

The history of petroleum in its practical applications belongs to modern times. For while the Fire-worshippers from India and the East resorted centuries ago to the district near Baku on

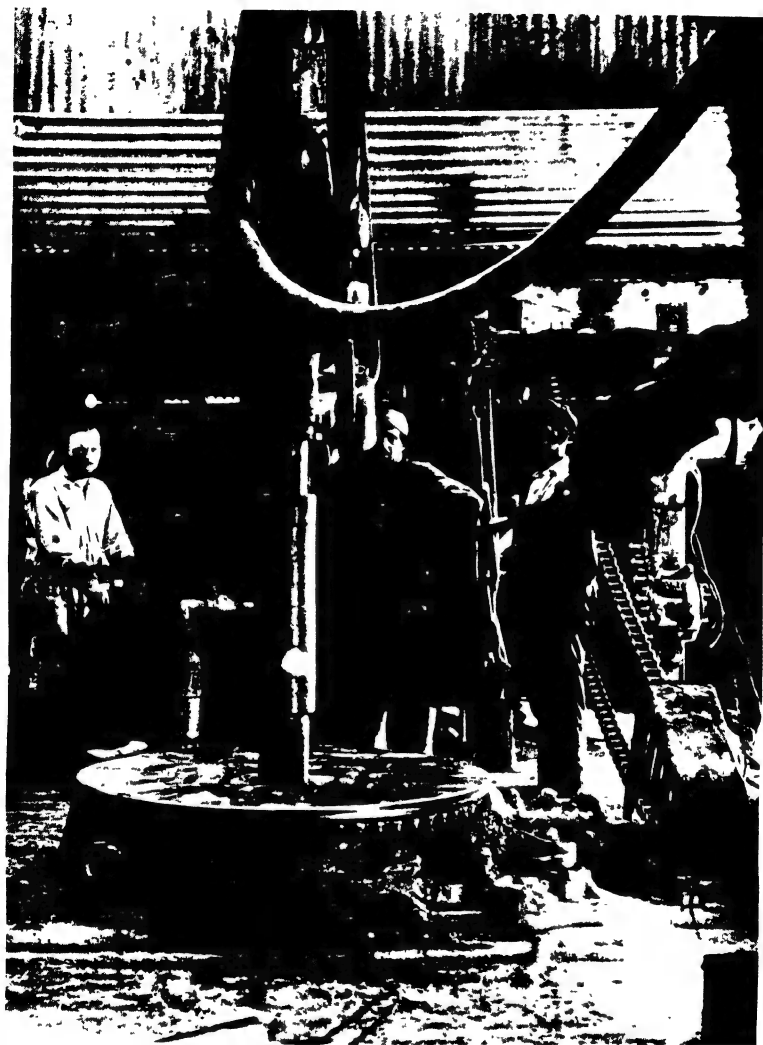


FIG. (69) —A ROTARY DRILL

(By courtesy of the Anglo-Iranian Oil Co., Ltd.)

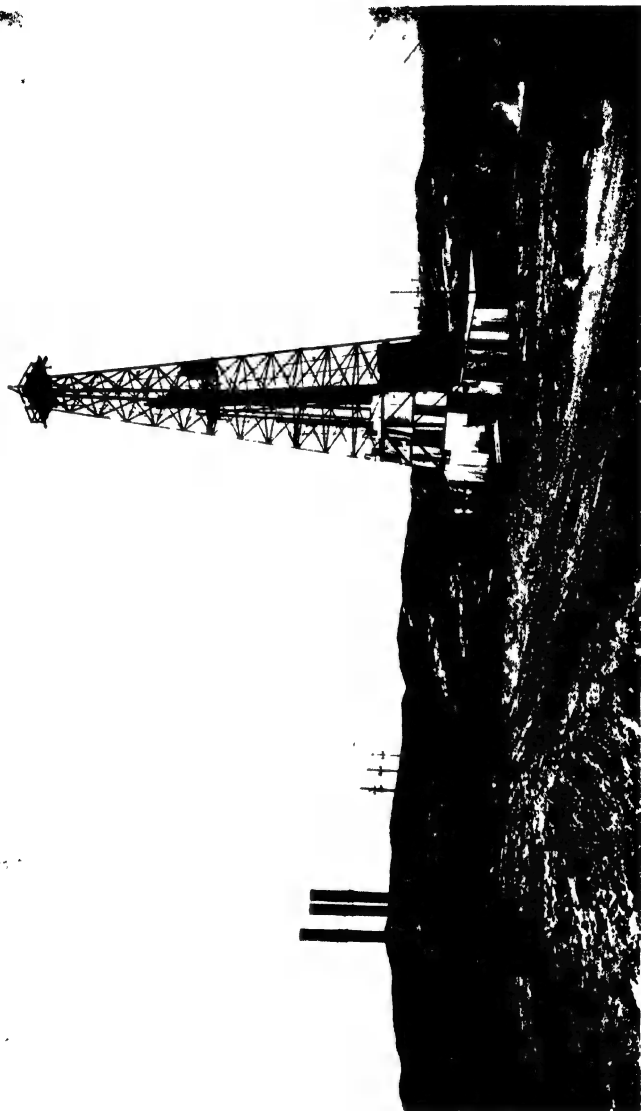


FIG 70—A ROTARY-TYPE DRILLING RIG IN SOUTH IRAN

(By courtesy of the *Anglo-Iranian Oil Co., Ltd*)

the Caspian Sea, where inflammable gas issued from the ground and where remains of some of their temples existed down to our own times, the use of the oil which was associated with the gas was of little practical importance.

The great petroleum industry of the United States began in 1859. Up to this time the oil which was used almost exclusively as a medicinal agent, both internally and externally, had been collected in a crude way from the water of the Seneca Lake in Allegheny County, New York, and other places. The production of burning and lubricating oils by distilling shales and other low-grade coal-like minerals was introduced in 1850 by James Young of Kelly, and it is probable that the recognition of the similarity between these oils and the natural petroleum led to experiments on the latter. It was soon found that on distillation a number of useful products could be obtained, including oil suitable for burning in lamps and a denser oil applicable as a lubricant and preservative to machinery.

Petroleum is usually associated with more or less salt water, and the strata which contain it are commonly charged with inflammable gas often existing there under enormous pressures. It may, however, happen that one of these products may exist without the others, and either salt water alone, or gas alone, may be obtained when oil was expected. The extraction of petroleum from the earth is accomplished by boring a hole to a suitable depth in the ground. The older method was to use a specially shaped tool which was alternately pulled up to a height and then let go so as to fall under the force of gravity. The hole so formed was lined with an iron pipe in order to strengthen it and prevent collapse of the earth. From time to time the tools, the shape of which depends on the type of rock being pierced, was lifted out and a "sand pump" introduced in order to remove pulverised rock and sediment. In the modern systems of boring a rotary bit, after the fashion of a twist drill, is used; by means of special devices the pulverised material is washed out continuously so that the drilling is not interrupted.

The wells thus sunk vary in depth in different oil fields, those in Pennsylvania ranging from 300 feet to 3700 feet; in some places they are, however, as deep as 10,000 feet. In a district which has been found to be productive the borings of wells soon multiply and the numerous derricks form a curious and striking feature in the landscape.

The type of country in which oil-fields are found varies considerably. In North America, for example, the Pennsylvanian oil-fields are situated among well-wooded hills, while the Californian wells are sunk in a district which is largely desert. The geological character of the rocks from which the oil is extracted is also different in these regions. In Pennsylvania the oil-bearing sandstone rocks belong to the Devonian system below the carboniferous series, while the Californian oil is derived from Eocene and Miocene beds, and that of Texas also from other formations more recent geologically than those of Pennsylvania. In no case is the oil deposit found in contiguity with beds of coal or shale, but in cavities generally, although not always, not in communication with one another. This is important to remember in connection with the question as to the origin of petroleum, which will be briefly discussed on a later page.

Turning now from the western hemisphere toward the east, the great Russian oil-field, extending through the Caucasian region chiefly along the shores of the Caspian Sea, is of the utmost commercial importance.

From prehistoric times this district has been the resort of all the East for the sake of the oil exuding from the ground. The inflammable gas which escapes in so many places was naturally the wonder not only of the natives, but of numerous pilgrims from afar.

Jonas Hanway, an English merchant in the reign of George II, visited the Caspian, and on his return, published in 1754, *An Account of British Trade over the Caspian Sea*. In this book he gave an interesting account of the phenomena which had attracted the Fire-worshippers from Persia and India for many centuries. The worshippers in Hanway's time all came from Bombay, the home of so many of the Parsees, the last disciples of Zoroaster. The ruined remains of the temples in which the priests tended the eternal flames which were the object of devotion existed in the neighbourhood of Baku down to our own times. These were described by Mr. Arthur Arnold (afterwards Sir Arthur Arnold), M.P. for Salford, who visited the district in 1875¹ but it is almost unnecessary to add that the pilgrims who now visit this region are attracted by considerations altogether different from those which brought the followers of the Magi.

The history of the commercial development of the Russian

¹ *Through Persia by Karavan*. London, 1875.

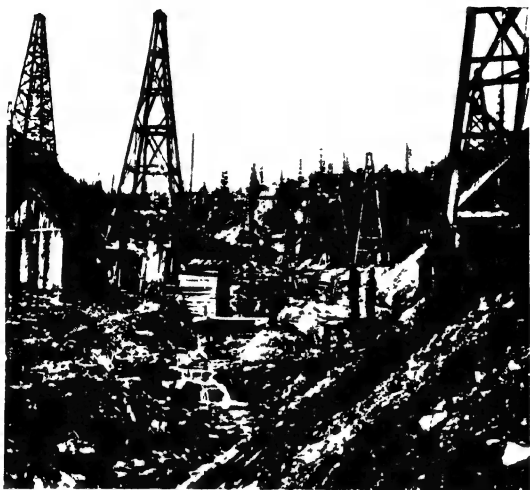


FIG 71 —TRIUMPH HILL, ON THE ALIEGHANY RIVER,
PENNSYLVANIA



FIG 72 —SPINDIE TOP, NEAR BEAUMONT, TEXAS



FIG 73 —BAKERSFIELD, CALIFORNIA

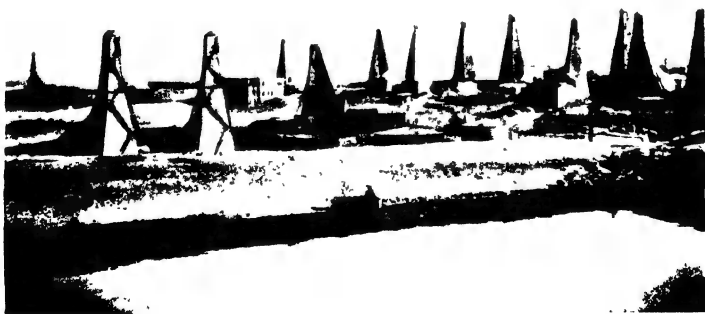


FIG 74 -- BINAGADI, NEAR BAKU, CASPIAN
AMBAR OR EARTH STORAGE RESERVOIR CONTAINING CRUDE OIL IN
FOREGROUND

oil-fields is comparatively simple, and the chief steps in its progress can be readily traced. When Baku became Russian territory, in the early part of the nineteenth century, having been taken from Persia, the extraction of oil was made a crown monopoly. The result of this was that the trade grew very slowly, and in the meantime American oil found its way into all the markets of the world. The monopoly at Baku was maintained down to 1872, but though the restriction was then removed an excise duty was imposed, which for five years longer served as an impediment to free production.

The rapid expansion of the Russian oil industry owes almost everything to the influence of the two brothers Robert and Ludwig Nobel.¹ Up to their time oil had been carried from the wells to the refineries in barrels, and the refined oil to the Russian consumer also in barrels. In place of this slow and costly system the use of pipe lines for transmitting the crude oil, the introduction of tank steamers on the Caspian in 1879, tank barges on the Volga, the subsequent establishment of tank cars on the Russian railways, and the provision of storage tanks at convenient points on the railways all over the country are due to the initiative of the Nobel Brothers.

"After that of Russia the petroleum industry of the districts of the Carpathian range next claims attention by its importance and antiquity. On the northern slopes will be found the oil-fields of Galicia²; while on the south-eastern and southern slopes of the southern Carpathians or Transylvanian Alps lie the important deposits of Rumania and the less-known fields of Bukovina and Hungary. . . . The petroleum industry in this country is of considerable antiquity. The earliest historical records show that oil was collected in a primitive fashion and used as a cart grease from very early times, and old timbered oil-wells still existing in Galicia and Rumania indicate that this practice prevailed to a considerable extent" (Redwood's *Petroleum*, Vol. I). The older wells were dug out, but modern methods of boring were introduced about 1881, and since then the development has gone on steadily, although production seems to have fallen off recently. The petroleum deposits of Rumania are continuous with those of Galicia; they are also supposed to be of about the same age as the petroleum-bearing beds of the

¹ Alfred Nobel, a third brother, was the inventor of dynamite. See "Explosives."

² Now part of Poland.

Caucasus with which they are said to be continuous (Redwood). The total Rumanian production was estimated in 1934 at upwards of eight million tons.

In consequence of the general association of the oil with gas confined in the oil-bearing rock or sand under pressure it frequently happens that when the rock is pierced the oil is forced up the bore-hole with great violence, producing a fountain of oil.

Many of these fountains which are very frequent in the Baku district have been described by the late Charles Marvin in his *Region of the Eternal Fire*, published in 1888, and we cannot do better than quote his account of the impressive spectacle exhibited by the famous Droobjba fountain in 1883. He says, p. 211, "The oil was flying twice the height of the great Geyser in Iceland, with a roar that could be heard several miles round. When the first outburst took place the oil had knocked off the roof and part of the sides of the derrick, but there was a beam left at the top against which the oil broke with a roar in its upward course, and which served in a measure to check its velocity. The derrick itself was 70 feet high, and the oil and the sand, after bursting through the roof and sides flowed fully three times higher, forming a greyish black fountain, the column clearly defined on the southern side, but merging into a cloud of spray thirty yards broad on the other. A strong southerly wind enabled us to approach within a few yards of the crater on the former side, and to look down into the sandy basin formed round about the bottom of the derrick where the oil was bubbling and seething round the stalk of the oil-shoot like a geyser. The diameter of the tube up which the oil was rushing was ten inches. On issuing from this the fountain formed a clearly-defined stem about eighteen inches thick, and shot up to the top of the derrick, where in striking against the beam, which was already worn half through by the friction, it got broadened out a little. Thence, continuing its course more than 200 feet high, it curled over and fell in a dense cloud to the ground on the north side, forming a sand bank, over which the olive-coloured oil ran in innumerable channels towards the lakes of petroleum which had been formed on the surrounding estates. Now and again the sand flowing up with the oil would obstruct the pipe, or a stone would clog the course; then the column would sink for a few seconds lower than 200 feet, to rise directly afterwards with a burst and a roar to 300. . . . Some idea of the mass of matter



FIG 75 - GROSNIK (S RUSSIA) OIL FOUNTAIN, AKHWERDOFF No 7
FOUNTAIN SPOUTING

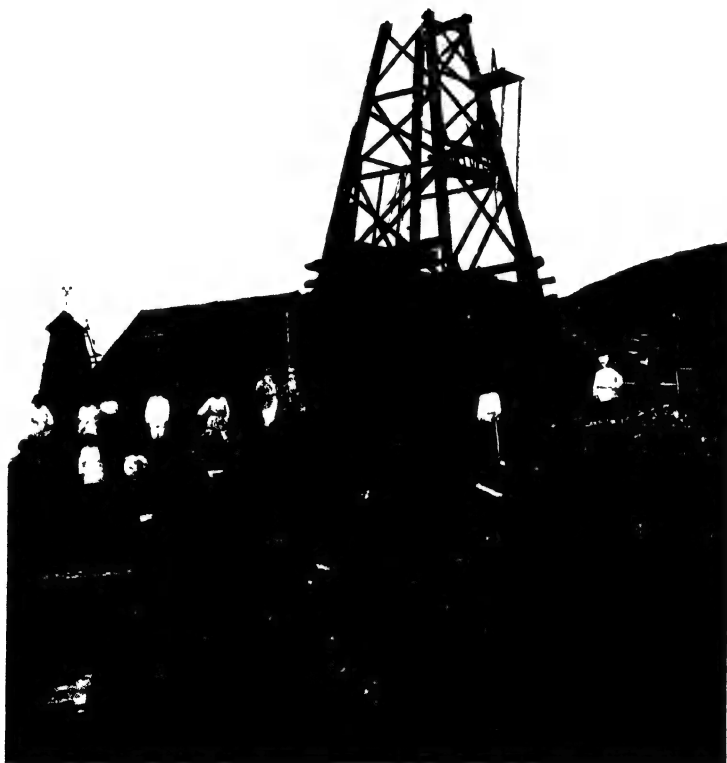


FIG 76 GROSNI (S. RUSSIA) DERRICK AFTER DESTRUCTION BY OIL
FOUNTAIN, AKHWERDOFF No 7

thrown up from the well could be formed by a glance at the damage done on the south side in twenty-four hours—a vast shoal of sand having been formed which had buried to the roof some magazines and shops, and had blocked to the height of six or seven feet all the neighbouring derricks within a distance of fifty yards.” The fountain belonged to a small Armenian Company, the Droojba, having ground enough to establish the well, but nothing to spare for reservoirs. Consequently all the oil flowed away on other people’s property and the owners of the well were ruined. This oil volcano was estimated to have thrown up from 1,600,000 to 2,000,000 gallons of oil every day from the first outburst which occurred on September 1st. In the middle of November it was still spouting at the rate of 240,000 gallons a day.

The pictures 75 and 76 give an idea of the sort of scene Marvin describes. Grosnic is situated north of the Caucasian mountains in country occupied by the Terek Cossacks. In the first picture the fountain is shown, having pierced the top of the derrick. The second picture shows the destruction wrought by the jet of oil which, after the fountain has subsided, continued to flow down a channel across which one of the workmen is seen astride.

In such cases there is usually an immense loss of oil and gas. Attempts are usually made, not always with success, to control the outflow by means of an iron cap with appropriate valves by which the stream of oil can be directed into a reservoir or tank.

One important oil-field further east exists in Burma, and is interesting to English readers as it exists in British territory. A very large proportion of the oil comes from the rich district of Yenangyoung, where for many generations hand-dug wells were worked by a class of hereditary oil winners under the Burmese kings. The rights of these people were recognised by the British Government after the annexation of Upper Burma, and a certain area was reserved for them in which they were annually allotted oil-well sites. In most cases they sold or leased these sites to the Oil Companies which introduced the American methods of drilling. Most of the oil existed under high gas pressure, so that when a well was bored into the oil enormous quantities gushed out.

The upper sand has now been exhausted and with it the gas pressure. Wells have now to be driven down to much greater depths and pumping is necessary, but the local experts are of

opinion that there are numerous sands, one below another, in the district. The oil from the field used to be carried to the refineries, which are situated in the immediate neighbourhood of Rangoon, solely by barges towed down the Irawaddy River. The Burma Oil Company some years ago constructed a pipe line underground the whole distance.

Burma petroleum contains a very high percentage of wax, and this has been the cause of much difficulty in pumping the oil through the pipe lines, by reason of its viscosity.

The petroleum obtained from the Koetei district in Borneo has become specially important in consequence of being found to contain a large quantity of the hydrocarbons of the benzene series, including benzene, toluene, xylene, and mesitylene, beside members of the naphthalene series. The less volatile portions, like some of the Russian oils, are optically active.

The rapidly increasing demand for petroleum products has resulted in a search for new oil-fields, and a number of these have been discovered, of which the ones in South America, in Iraq, and in Persia (Iran) deserve special mention. The following table gives the total world production of crude petroleum for the years 1911 and 1934; it shows not only the tremendous increase which has taken place but the new sources of oil which have been discovered. The figures can only be regarded as approximate, since different data are quoted in different places, but they give a satisfactory idea of the position; 1 ton is roughly 270 gallons.

WORLD'S PRODUCTION OF CRUDE PETROLEUM IN TONS

Source.	1911.	1934.
United States	29,400,000	130,000,000
Russia	9,000,000	26,400,000
Venezuela	?	19,400,000
Rumania	1,540,000	8,300,000
Persia	?	7,400,000
Dutch East Indies . .	1,670,000	6,000,000
Mexico	1,870,000	5,000,000
Colombia	?	2,350,000
Argentina	?	2,000,000
Peru	186,000	2,000,000
Trinidad	?	1,560,000
India	900,000	1,260,000
Other countries (approx.)	1,950,000	750,000
Total	46,500,000	212,400,000



FIG. 77 PIPE-LINE, NEAR MUSJID-E-SULAIMAN, IRAN
(Photograph also shows storage tank and character of country)
(By courtesy of the Anglo-Iranian Oil Co., Ltd.)

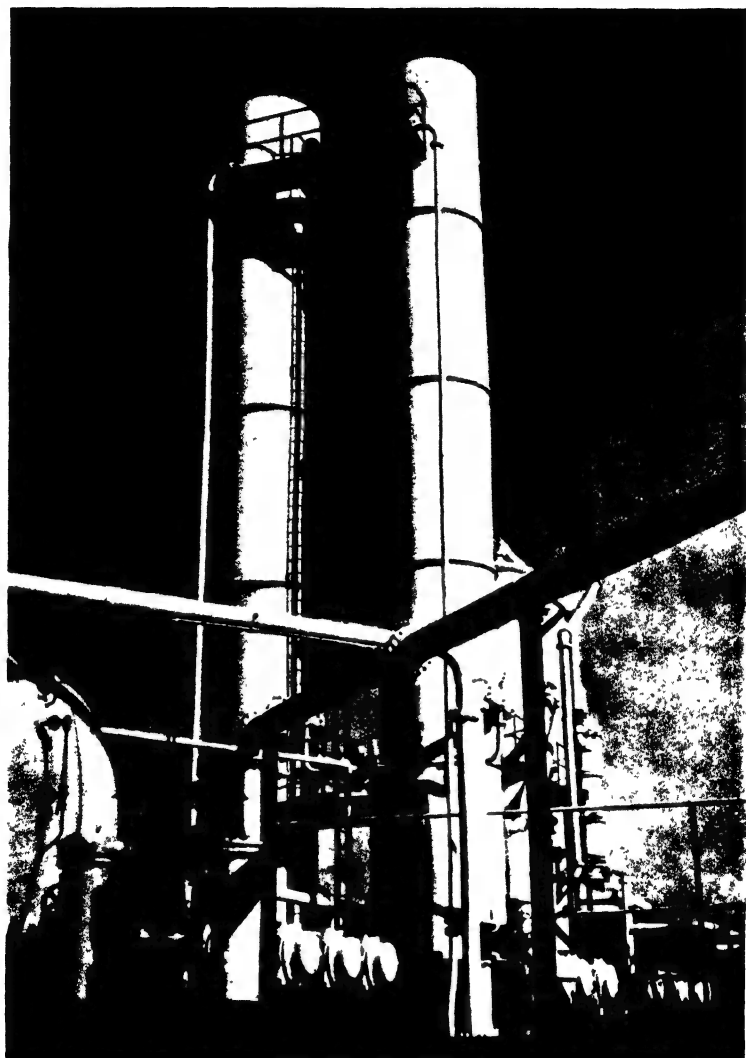


FIG. 78.—PLANT FOR REMOVAL OF GAS FROM PETROLEUM, MUSHD-I-SULAIMAN OILFIELD

(By courtesy of the Anglo-Iranian Oil Co., Ltd.)

Crude petroleum is an unattractive brown or nearly black liquid which floats on water. Though inflammable and when blown into spray mixed with a sufficient supply of air it may be employed in locomotive engines or under boilers for raising steam, it is not well fitted for burning in lamps, as a source of light, owing to its viscosity and the presence of impurities. In order to obtain from it various useful products it requires to be submitted to distillation. The refineries in which petroleum is thus dealt with are usually situated at a considerable distance from the oil-field. Consequently the question of conveyance becomes one of great practical importance.

During the first ten years, or thereabout, of the American oil industry the crude oil was carried chiefly in barrels from the wells to the refineries, but as the business grew this method was not only expensive, but quite inadequate to deal with the very large quantities of oil obtained. The greater part of the oil has long been conveyed by means of lines of iron pipes which commonly run alongside the railway track. Many of the oil-wells in Asia are situated in remote districts where refining is almost impossible, the crude oil is therefore sent to the coast by pipeline, either for refining there or for conveyance by specially constructed tank steamers to Europe. One of the most remarkable of these pipes is the one recently completed from the new Iraq oil-field at Kirkuk to the coast of Palestine (Haifa) and of Syria (Tripoli); its total length is over 1100 miles.

Arrived at the refineries the oil has to undergo the process of distillation. As everyone knows, this process consists in heating the liquid in some kind of boiler or "still" with a head which confines the vapour given off and conducts it into a pipe or series of pipes, cooled, if necessary by water, where the vapour is condensed into the liquid state, and is run into a receiver.

The older form of still consisted of a large cylindrical iron vessel, capable of holding between 50,000 and 60,000 gallons; it was heated by burning some of the waste oil, and as the temperature rose the liquids distilling between different ranges of temperatures, thus giving a series of "fractions," was collected in separate vessels. This method of distillation is now giving place to one in which the process is continuous, all the fractions being drawn off simultaneously (see Fig. 79). The crude oil is passed through a long pipe in a furnace and the resulting liquid and vapour is passed into a vertical rectifying column, down

which flows some low boiling-point distillate (gasoline or petrol). The process of rectification takes place in the column, similar to that occurring in liquid air rectification (p. 248), the separate fractions accumulating at different points from which they are continuously drawn off; the lower boiling-point fractions come off from the top of the column, and the higher boiling-point portions towards the bottom. Steam is introduced, as shown, to facilitate the vaporisation of volatile constituents.

There are in general four main fractions: the first and lightest portions of the distillate, after chemical treatment to remove sulphur and other impurities, is known as petrol or gasoline, and is the main source of motor-car fuel. The second fraction forms the basis of kerosene or paraffin oil, used in lamps; this is followed by gas oil, the use of which will be explained later, and finally by an oil which on cooling separates paraffin wax and leaves a thick liquid suitable for inclusion in lubricating oil. The residue run off from the very bottom of the rectifying column is either bitumen or pitch, depending on the nature of the original petroleum. Sometimes other fractions are collected; for example, in between the petrol and kerosene fractions "white spirit" is obtained, which is employed for dry-cleaning and for thinning paint. The approximate proportions of the different main fractions resulting from the distillation of 100 parts of American petroleum are as follows:

Petrol	42 parts
Kerosene	5 "
Gas oil	40 "
Lubricating oil	3½ "

The petrol constitutes 60 per cent of the total value of the distilled oils.

At one time the gas oil was used for burning under boilers, but this serious wastage was stopped when the process of "cracking" was invented; this consists in heating the oil to a high temperature, when it is converted to a large extent into oils of greater volatility suitable for admixture with petrol. In the cracking process the complex molecules of hydrocarbon present in the gas oil are broken up into simpler hydrocarbons. Two main methods of cracking are in use: these are called "liquid" and "vapour" phase cracking, respectively. As the names imply, in the former the liquid oil is heated, the temperature being

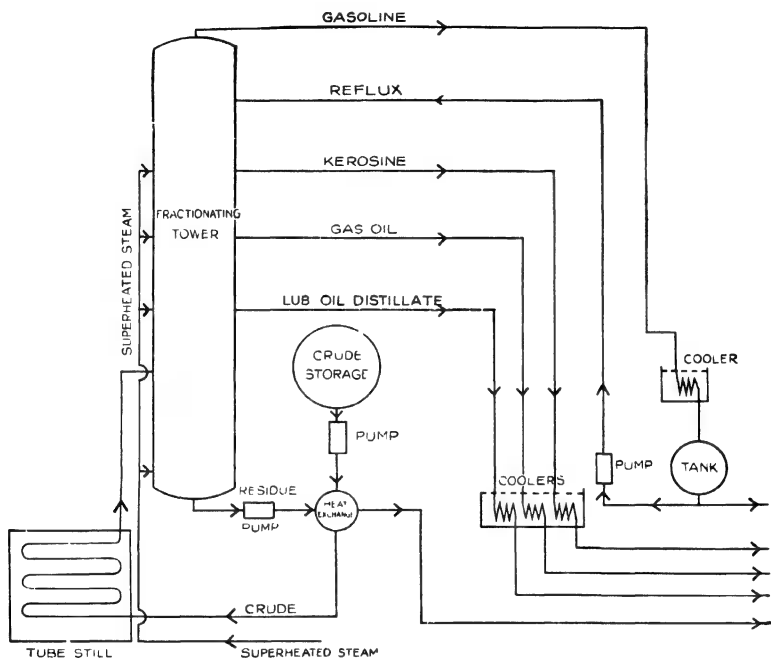


FIG 79—DIAGRAMMATIC REPRESENTATION OF CONTINUOUS PROCESS FOR PETROLEUM DISTILLATION

(From "Chemistry in Commerce", article by E. A. Hartup, Shell-Mex, Ltd., by courtesy of the author)

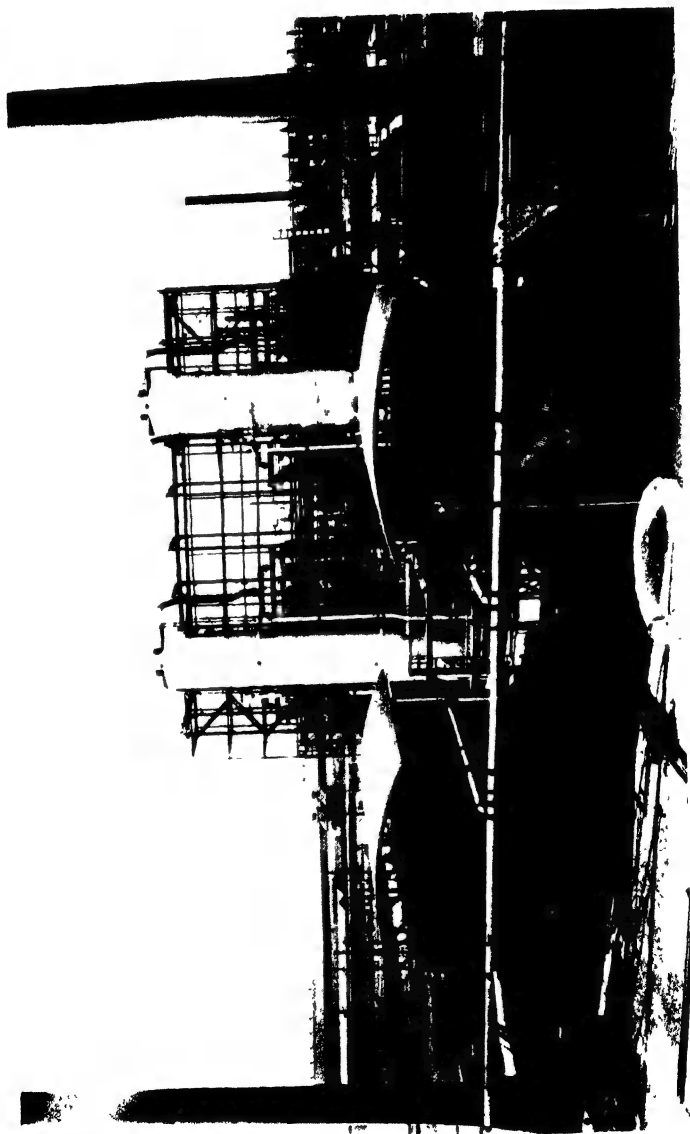


FIG. 80.—DISTILLATION UNIT, ABADAN REFINERY, IRAN

(By courtesy of the Anglo-Iranian Oil Co., Ltd.)

between 360° and 480° C. according to the type of plant used ; in the vapour phase method a much higher temperature, 600° C., is employed so that the oil is completely vaporised. There is a difference of opinion as to which process is best, and both seem to have advantages ; the liquid phase method gives a bigger yield of petrol, but that obtained by vapour phase cracking has better "anti-knock" properties.¹ Since these qualities are now obtainable in other ways there seems a tendency for liquid cracking to re-establish itself, although it appeared at one time that it would be ousted by the process in which the gas-oil vapour was cracked. The importance of cracking will be realised when it is stated that about one-half of the United States output of petrol (gasoline) consists of cracked spirit, and that it constitutes about one-third of the whole world's supply.

One of the difficulties concerning cracked spirit is that it contains substances which are easily oxidised on exposure to air, forming gummy materials capable of clogging the valves of the cylinder and the carburettor ; these are removed to some extent by treatment with sulphuric acid. In addition, various "gum-inhibitors" have been discovered, which prevent oxidation and so retard gum formation. The inhibitors consist of various phenols and amines, which are synthetic products from coal tar.

One of the great problems of the petroleum industry, which now seems to be on the way to solution, is the question of finding some use for the vast quantities of gas accompanying petroleum oil. On the average 60 cubic feet of gas are evolved for every gallon of crude oil, and in the United States some two thousand billion cubic feet are given off per annum, which at one time was nearly all allowed to go to waste. At the present time the gas is first compressed and scrubbed with a special oil to remove petrol ; it is then further compressed and cooled when two very low boiling-point constituents, propane and butane, are liquefied and collected in cylinders. These liquids vaporise quite easily, and the resulting gases burn readily with a considerable evolution of heat. The cylinders of propane are sold for domestic purposes, and are being employed on a large scale in the remote country

¹ "Knocking" or "pinking," with which motorists are familiar, is due to premature detonation of the petrol vapour in the cylinder leading to loss of efficiency. Some petrols have little tendency to knock, and this quality, known as "anti-knock" is aimed at in the modern blending of motor spirits.

districts of the United States for heating and lighting purposes. The butane has to be warmed slightly to gasify it, and so it is not so suitable for domestic purposes, but it is being used as a fuel in industry and also to enrich coal gas.

Even after the removal of the petrol and other readily liquefiable hydrocarbons from the natural gas, there still remains a large quantity of methane which constitutes between 80 and 90 per cent of the original gas. As already described (chapter XIV) the Standard Oil Company of America is developing a method for obtaining hydrogen from it on a large scale. This hydrogen is being used to "hydrogenate" certain of the petroleum distillates, and in this way lubricating oil constituents, with exceptionally valuable properties at the high temperature of the internal combustion engine, are being obtained.

Another possibility which is being considered, and which is already being used to some extent, is to bring about a sort of reversed cracking process, so that the simple hydrocarbon gas methane, CH_4 , becomes a more complex one which is liquid at ordinary temperatures and can be used as petrol. The process involves heating the natural gas to a temperature of nearly 1000°C. , which is much higher than that used in the ordinary cracking of gas oil, without using any high pressure but possibly in the presence of a suitable catalyst. It is claimed that from two to three gallons of petrol spirit can be obtained from a thousand cubic feet of gas. This method of amplifying our petrol supplies is likely to attract much attention in the future, as the sources of petroleum become gradually exhausted.

COMPOSITION AND USES OF PETROLEUM

Before attempting to enumerate the various uses to which petroleum and products from it are applied, it will be well to take a survey of the general nature of these products. The compounds which have been identified among the products of distillation are very numerous, and in the following table it has been thought sufficient to include only those which are the most abundant and characteristic. They are ranged according to their physical condition at the common temperature of the air, and according to their chemical composition. The substances mentioned are all compounds of carbon and hydrogen only, and the chemist speaks of them as hydrocarbons, a term which has been already used, as it is almost self-explanatory.

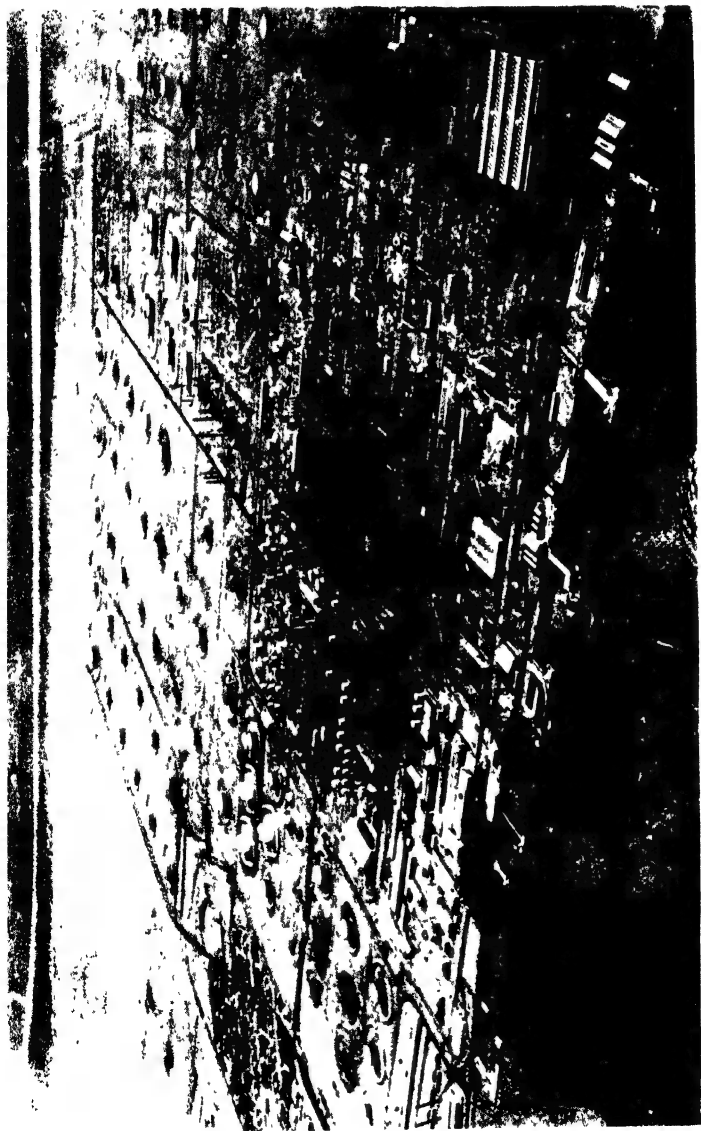


FIG. 81.—AERIAL VIEW OF THE ABADAN REFINERY, ANGLO-IRANIAN OIL CO., LTD

(By courtesy of the Anglo Iranian Oil Co., Ltd.)

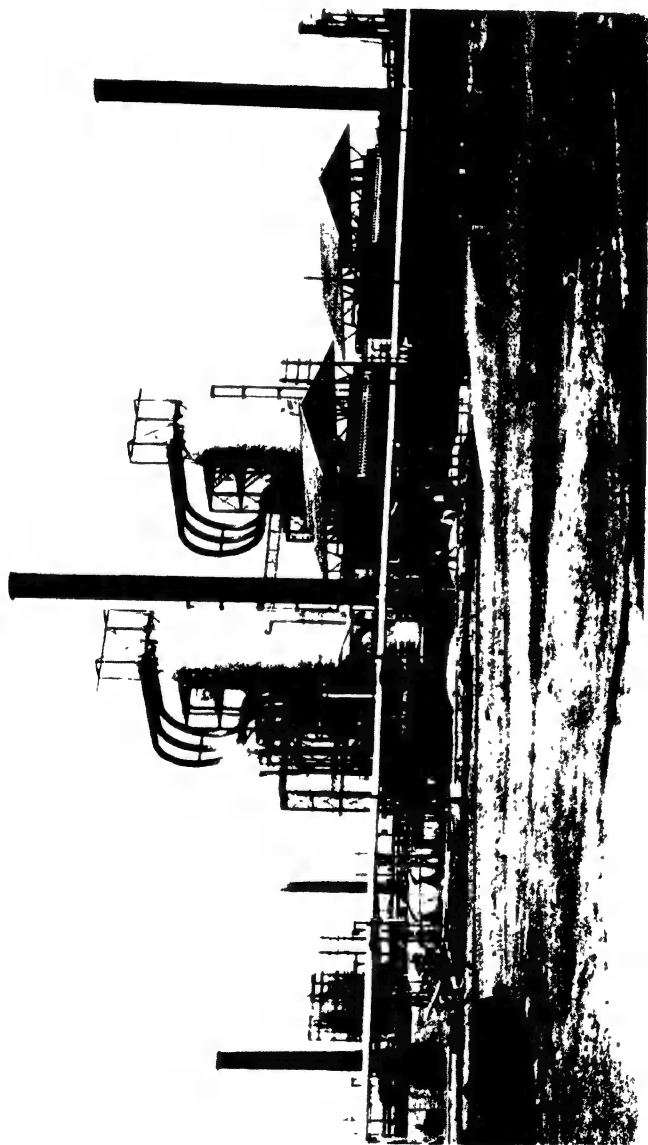


FIG 82 —DETAIL OF REFINING PLANT AT ABADAN
(By courtesy of the Anglo-Iranian Oil Co. , Ltd)

With these compounds are associated in the natural oils minute quantities of substances containing nitrogen and sulphur, which, however, may be dismissed from further discussion at this point.

PENNSYLVANIAN PETROLEUM

GASEOUS

Paraffins.		Olefines.	
Marsh-gas	CH_4	Ethylene	C_2H_4
Ethane	C_2H_6	Propylene	C_3H_6
Propane	C_3H_8	Butylene	C_4H_8
Butane	C_4H_{10}		

LIQUID

Paraffins.	Formula.	Boiling point C.
Pentane (normal)	C_5H_{12}	About 38°
(iso)	"	30°
Hexane (normal)	C_6H_{14}	69°
(iso)	"	61°
Heptane (normal)	C_7H_{16}	97.5°
(iso)	"	91°
Octane (normal)	C_8H_{18}	125°
(iso)	"	118°
Nonane	C_9H_{20}	136°
Decane	$\text{C}_{10}\text{H}_{22}$	158°
Endecane	$\text{C}_{11}\text{H}_{24}$	182°
Dodecane	$\text{C}_{12}\text{H}_{26}$	198°
Tridecane	$\text{C}_{13}\text{H}_{28}$	216°
Tetradecane	$\text{C}_{14}\text{H}_{30}$	238°
Pentadecane	$\text{C}_{15}\text{H}_{32}$	258°
Hexadecane	$\text{C}_{16}\text{H}_{34}$	280°
Octadecane	$\text{C}_{18}\text{H}_{38}$	320°
?	?	

SOLID

Paraffin,	$\text{C}_{27}\text{H}_{56}$,	melting about 60°
"	$\text{C}_{30}\text{H}_{62}$	" " 66°
	etc.	etc.

The American oils consist chiefly of paraffins, there being a relatively large proportion of lighter and simpler ones which have low boiling-points; Russian oil, however, yields a smaller proportion of the lighter and more volatile portions of spirit. This oil is characterised by the presence of a considerable quantity

of compounds called *naphthenes*, which have many of the characteristics of paraffins, but their formulæ are written in the form of a ring (see p. 311) and so they are known as cyclo-paraffins. They have compositions represented by C_6H_{12} , C_7H_{14} , C_8H_{16} , etc., and their boiling-points range from about $69^\circ C.$ to near $250^\circ C.$ Beside the naphthenes Russian petroleum is believed to contain small quantities of benzene and toluene.

The first and most important use alike of the crude natural petroleum and of portions separated by distillation is as a source of power, that is, as some form of fuel.

The fluid residue from the refineries has for many years been employed under the name *ostatki*, as fuel on the locomotives in Southern Russia, and on the steamers on the Black Sea and Caspian. The use of liquid fuel has many obvious advantages coupled with some disadvantages. First of all it is composed almost entirely of the combustible elements carbon and hydrogen, while bituminous coal contains not only oxygen, but a considerable quantity of mineral matter which is left in the form of ash or clinker after burning.

A further advantage possessed by a liquid is that it occupies much less space than an equal weight of a solid in lumps, and may be stowed in bunkers of any shape or in spaces which could not be utilised for coal. The bunkers can also be filled by simple pumping with the expenditure of much less labour, the flame produced by burning is instantly available, and with a properly constructed furnace no smoke need be produced. There are also no ashes to be cleared out from the furnace and removed by the stoker.

In order to burn a thick liquid like natural petroleum it is necessary to distribute it in the form of a spray, and a great deal of ingenuity has been expended in contriving burners for this purpose. In many forms of "atomiser" the oil is sprayed by means of a jet of steam into a chamber where it finds the air requisite for combustion, and by regulation of the oil supply a blue smokeless or a smoky flame may be produced at pleasure. In other forms of jet the oil is pulverised by being forced under pressure through a small orifice of peculiar construction.

Reference has already been made to the chief products of petroleum distillation, and a few further remarks may be added here. The lowest boiling fraction, including the hydrocarbons from C_5H_{12} to C_7H_{16} , approximately, is sometimes separated and

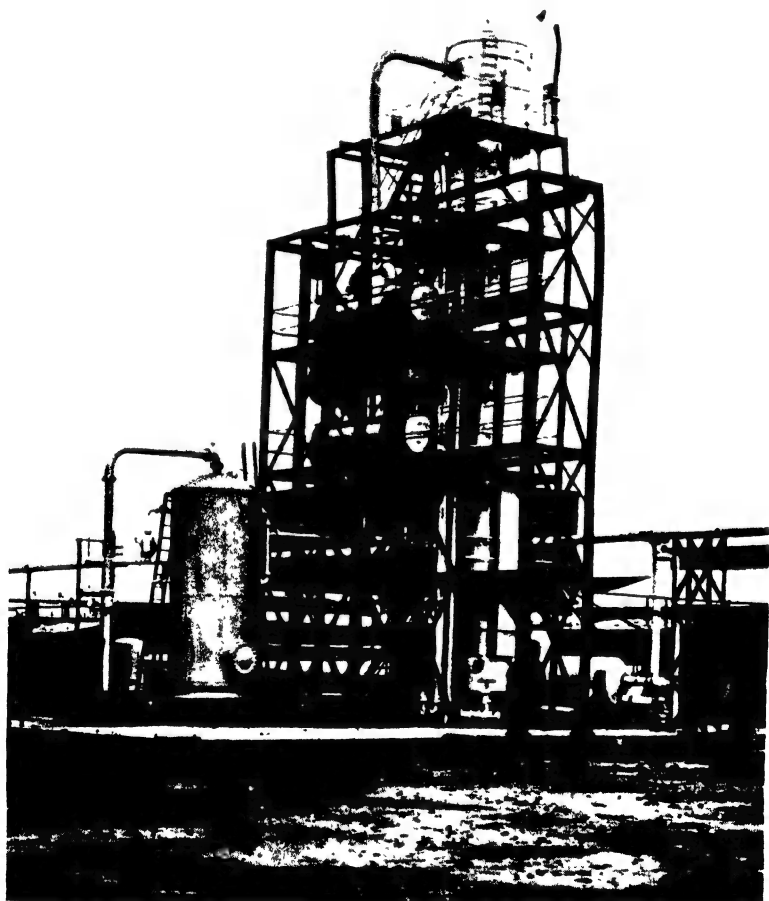


FIG 83 ABADAN PETROLEUM REFINERY

(By courtesy of the Anglo-Iranian Oil Co., Ltd.)

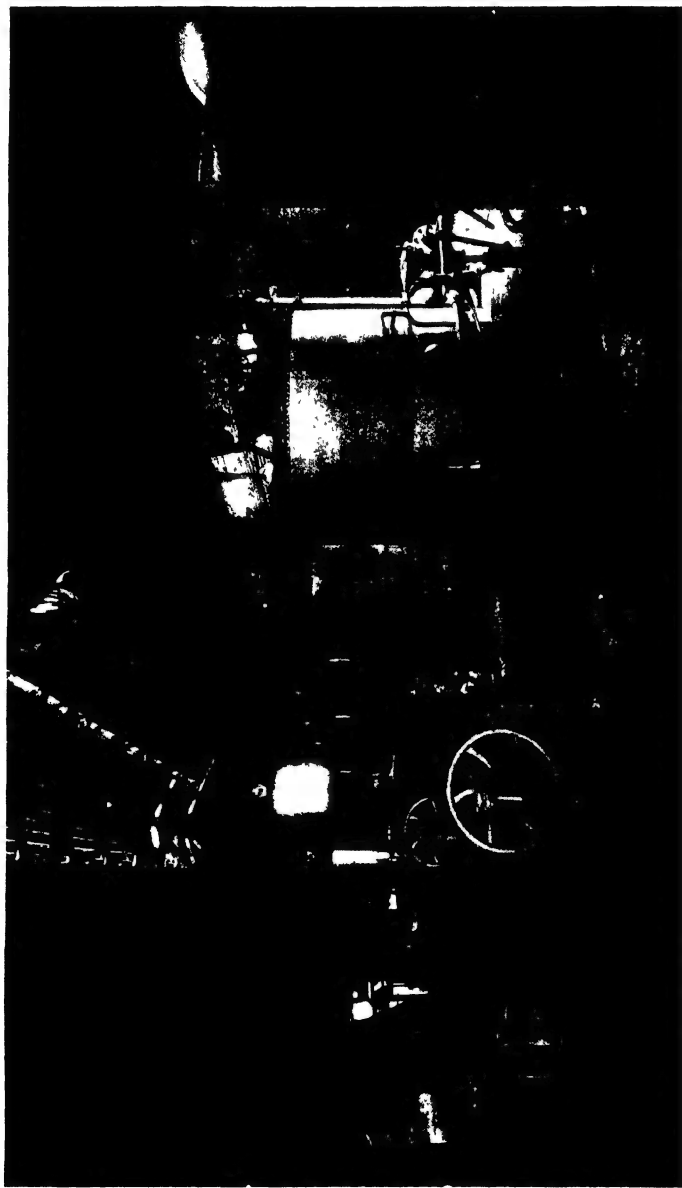


FIG 84.—CARBURETTED WATER GAS PLANT GAS LIGHT AND COKE COMPANY

sold as *petroleum ether*, *rhigoline*, or *benzoline*; it has been used as a local anæsthetic, if especially rich in the simplest hydrocarbons, and has been employed for producing the "air-gas," at one time much used in country houses. Ordinary petrol or gasoline includes from C_5H_{12} to $C_{11}H_{24}$ or even higher; it is used extensively as motor spirit, for cleaning purposes and as a solvent. White spirit or naphtha extends from about C_8H_{18} to $C_{15}H_{32}$, whereas *paraffin oil*, *kerosene*, or *colza oil* is the product containing the hydrocarbons from $C_{10}H_{22}$ to the end of the series of liquids quoted above. The lubricating and gas oils lie in between the liquids and the solids, possibly including some of the latter.

Paraffin wax is a familiar solid used for making candles and for other purposes. Vaseline a well-known semi-solid or jelly-like substance used for protecting metals from rust and corrosion, and as an ointment or dressing in surgery is also obtained from the lubricating oil fraction of the petroleum distillate.

An important use of petroleum oil is in connection with the production of gas for domestic purposes; it is the custom at the present time in up-to-date gas works using vertical retorts to pass steam through the hot coke in order to obtain water gas (p. 242) which mixes with the coal gas. The calorific power of water gas is not up to the required standard, and so a certain amount of "cracked" gas from petroleum is used to enrich the water gas. For this purpose the gas undertakings in Great Britain utilise about 50 million gallons of oil per annum. It is interesting to note that this "carburetted water gas" was originally valued because of its illuminating power, but fortunately it also has the good heating qualities which are now in demand.

Before concluding this chapter with a short section on the origin of petroleum, the following figures showing the amounts used in some of the most important consuming countries may be quoted.

CONSUMPTION OF PETROLEUM (1934) IN TONS

Country.	Tons Consumed.
United States	125,000,000
Russia	13,500,000
Great Britain	10,500,000
France	5,600,000
Canada	4,800,000
Germany	3,900,000

It will be seen that the United States not only produce the largest proportion of the world's oil, but they are also by far the largest consumers.

ORIGIN OF PETROLEUM

Everyone is familiar with the idea that common coal, in all its different varieties, is a product of chemical change, taking place through long geological periods, in masses of vegetable matter accumulated in certain strata of the mineral matters forming the crust of the earth. Concerning the origin of petroleum there is, however, no such unanimity of opinion. Many speculations have been put forward from time to time, and without entering into much detail, these may be at once ranged under two main divisions.

The question is did natural oil result from purely chemical processes taking place in the earth, or did it result from the action of heat on the remains of organic beings, animal or vegetable ?

That rock oil may have been formed without the previous existence of living things is the view which was promoted chiefly by the famous Russian chemist Mendeléeff, and it has much to recommend it. Thus some deposits of oil are found in the most ancient Silurian rocks, where it is difficult to suppose a previous sufficient accumulation of organic matter.

The formation of hydrocarbons can be accounted for by supposing that the interior of the earth consists largely of compounds of carbon with such heavy metals as iron and manganese in a heated state. During the upheaval of mountain chains, and in times of superficial disturbance owing to contraction, water may penetrate through the crust of the earth and thus come into contact with these carbides, the hydrogen of the water uniting with the carbon, while the oxygen of the water forms oxides with the metals. From direct experiment on cast iron and on *Spiegel-eisen*, both of which contain iron and manganese united with carbon, it has long been known that this change is produced by contact of the metal with water or acids. This hypothesis harmonises also with what is known of the constitution of our earth, which is probably a metallic mass, having a thin earthy crust on the surface, like so many of the meteorites which fall from the skies. The mean density of the earth as a whole is about 5.5, that is to say, it would weigh 5.5 times as much as an

equal bulk of water. But the crust of the earth accessible to us consists of minerals which are generally not more than about twice as heavy as water, and therefore the interior must contain a large quantity of something much denser.

An alternative theory has been proposed more recently, about 1904, by Professor Paul Sabatier of Toulouse, whose discovery of the remarkable catalytic actions of certain metals has been referred to elsewhere (p. 213). He assumes that in the depths of the earth are found deposits of the alkaline metals, sodium, potassium, etc., as well as compounds of these metals with carbon. This assumption is less novel than might appear, if it were not remembered that Davy, a century earlier, had supposed that deposits of this kind might occur in the earth's crust, and had attributed volcanic explosions in certain cases to the entrance of water, with which as is well known they react violently.

Sabatier imagines that such deposits of metal may be the cause of the production of hydrogen, while their carbides in contact with water simultaneously produce acetylene. These two gases in variable proportions are then assumed to come into contact with one or other of the metals, nickel, cobalt, or iron, in a finely divided state and at an elevated temperature, the result being that by condensation of the acetylene alone or by union with hydrogen under the influence of the heavy metal a mixture of hydrocarbons results.

These may consist of (1) saturated paraffins as in the Pennsylvanian petroleum, or (2) cyclic paraffins such as occur in the Caucasian oil, or (3) a mixture containing also benzenoid hydrocarbons and unsaturated compounds, such as are found in the petroleum of Galicia and other districts. Sabatier does not pretend that other theories of the formation of these natural hydrocarbons are necessarily excluded, but he claims that no other theory serves to account for the diversity observed in the composition of petroleum from different regions, and especially for the production of the naphthenes.

On the other hand, the suggestion is offered that large masses of vegetable or animal matter may have accumulated in past geological times, that they may have undergone decay, and that subsequently a process corresponding to that which has given rise to coal gradually set in. Later a rise of temperature sufficient to cause complete chemical decomposition must be assumed, and this would cause the oil, and gas which would be formed at

the same time, to pass from lower to higher strata, and still be retained under the pressure of superincumbent rock.

Such a view is consistent with the fact that oils closely similar to natural oil are obtained by the action of heat on coal and shales as in the manufacture of paraffin oil from these materials.

It also would explain the existence of petroleum in so many cases in strata in which no animal or vegetable remains are found, and in fact the general distribution of petroleum in the crust of the earth without apparent connection with the geological age or character of the rocks in which it is found.

That petroleum may have originated in beds of animal or vegetable matter is rendered probable by the fact that certain varieties have the power of rotating a ray of polarised light, while nearly all contain an appreciable quantity of nitrogen in the form of nitrogenous bases similar to those which are derived from the distillation of coal or animal matter. A small quantity of sulphur in the form of an organic sulphide is also frequently present.

It is quite possible, in view of the variation in the composition and character of the oil found in different regions, that petroleum may have been produced from both mineral and organic sources.

There is, however, something fascinating in the idea that this valuable natural product may be actually in process of formation now and always from the body of the earth itself without the intervention of living beings.

There are, however, outstanding difficulties in respect to all these theories, and it is probable that it will be some time before the formation of the higher terms of the paraffin series (paraffin wax, ozokerite, etc.), and the differences of constitution between the American and Russian oils are fully explained.

CHAPTER XX

COAL-TAR

It seems a far cry from the black, sticky, and stinking liquid coal-tar to the brilliant or delicate colours adorning a lady's dress, to the perfume of the Tonquin bean, or the little white tabloid of aspirin or phenacetin which affords relief from pain.

But the black tar is the chemical ancestor of these and many other valuable products unknown to our grandfathers, and the business of extracting from it the intermediate substances which are more directly the parents of the dyes and other things is a matter of great national importance.

When coal is heated strongly in a closed vessel, so that it does not burn, it yields four chief products, viz. :

Gas.

Watery ammoniacal liquor.

Tar.

Coke.

At the gas works the first of these is the primary object of the manufacture, while the liquor and tar are spoken of as residuals, together with the coke which is left behind in the retorts. But in connection, specially, with the production of iron and steel the purpose in view in heating coal is not so much the production of gas as of the residual coke. The process is carried out in coke "ovens," and down to comparatively recent times the coke alone was preserved, all the gas and other volatile products given off were burned to waste. This, however, is no longer the case, and since the more general recognition of the value of the by-products most of the coke ovens of the present day are constructed so as to provide for collecting and so utilising what was formerly wasted.

The accompanying diagram shows in section the construction of what is known as a beehive oven. A number of these are always placed side by side with the object of economising heat and convenience of charging. Each oven is a brick structure lined with firebrick. There is an opening below by which the coal is charged into the oven and by which the coke when produced is withdrawn. The oven is filled up to the shoulder, giving a layer of coal about five feet thick, and the combustion is started at the top and proceeds downwards till the whole is deprived of volatile matter and the luminosity of the flame at the top practically ceases. During the burning the admission of air through the door is regulated by a damper or a movable brick. When the operation is over the coke is withdrawn and quenched with water. The oven while still hot receives a fresh charge of coal. This process yields a quantity of coke amounting to about 60 per cent of the coal, but while the coke is hard, lustrous, and

eminently fitted for use in the blast-furnace or foundry the 30 or more per cent of the volatile products are all lost.

The importance of saving the tar and the ammonia which are given off by coal, when heated, together with a large quantity of inflammable gas has led to an immense amount of invention, and an almost innumerable variety of ovens have been devised with the object of recovering and utilising these by-products. One of

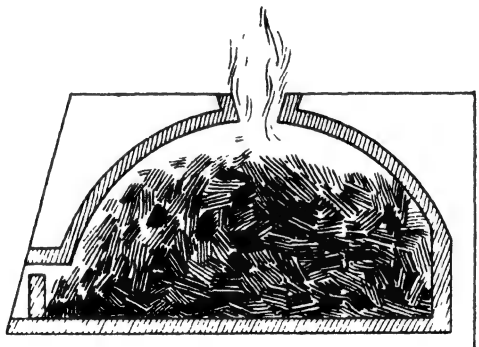


FIG. 85. THE BEEHIVE COKE OVEN

the first contrivances introduced was the coke oven known as Jameson's. This was shaped like a beehive, but the floor sloping forward was perforated with holes which opened into pipes underneath. These communicated with a large horizontal main which ran along the front of a series of ovens and in which tar and ammoniacal water collected. The gas was drawn forward by a pump and delivered into a gas-holder. The more modern ovens generally take the form of some modification of the Coppée oven, in which the principle is quite different. Instead of generating the requisite heat by the combustion of a portion of the coal the charge in these ovens is never brought into contact with air, but is submitted to a process of distillation by heating in closed chambers. The heat required is obtained by combustion of part of the gas given off by the coal within, and further economy is secured by making use of the regenerative principle, that is to say, the gas before being burnt and the air required to burn it are both heated by passage through ducts arranged between the retorts or ovens.

The modern type of coke oven may be 40 to 45 feet in length,



FIG. 80.—BECKER RECOVERY-TYPE COKE OVENS, NORMANBY PARK WORKS, SCUNTHORPE

(By courtesy of *The Woodhall-Deukham & Co., Ltd.*)

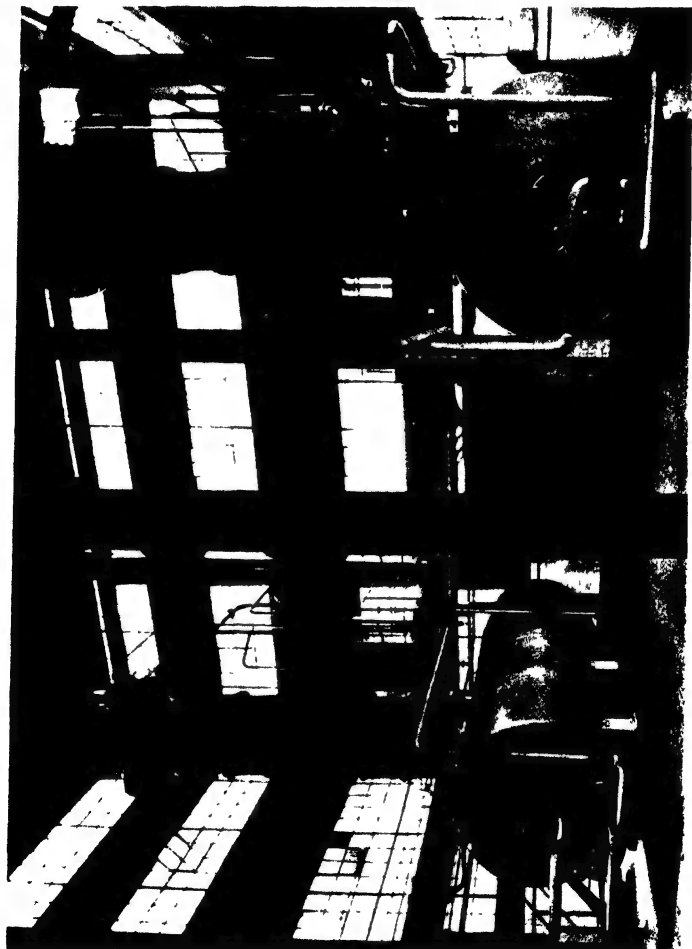


FIG 87—BENZOL STILL, LANCASHIRE STEEL CORPORATION, BY-PRODUCT RECOVERY PLANT, IRLAM

(By courtesy of The Woodhall Duckham Co., Ltd.)

from 13 to 20 feet high, and 14 to 18 inches wide ; a number are arranged side by side with heating flues in between, and owing to the comparative narrowness of the ovens the heat rapidly penetrates to the centre of the coal contained therein. The oven chambers have doors at each end so that after completion of the process the mass of coke can be pushed right out by means of a powerful ram. Each oven, of the dimensions mentioned, has an output of 25 to 30 tons of coke per day. Most by-product ovens in use at the present day work on a similar principle, although they are not all as large as that described, the modern Becker oven, and they generally differ only in the arrangement of the heating ducts, or flues, and the method used for pre-heating the air and gas supplied to the burners.

The coal is charged into the ovens from wagons which run on rails over the set of ovens. The gas and other volatile products given off from the coal are conveyed away through pipes to a series of collecting wells and purifiers and a gas-holder. Part of this gas, having thus deposited nearly all the tar and ammoniacal liquor, is brought back to a series of burners where, with admixed air, it is burnt in the spaces between the ovens, the walls of which are thus raised to a bright red heat. The products of combustion, chiefly carbon dioxide and water vapour, after being used to pre-heat the entering gas and air, pass on to the chimney stack. By means of an apparatus of this kind great economy is secured. There is a yield of about 70 per cent of coke equal in quality to the bee-hive coke, together with a proportion of the gas and all the tar and ammonia which the variety of coal used is capable of yielding.

In some districts where the manufactures can be combined together the surplus gas from the coke ovens, of a quality which is up to the present say standard of heating, is delivered into the ordinary coal-gas mains.

For the purpose of generating combustible gas a variety of systems have been adopted by which air in limited quantity is drawn or driven through a mass of red-hot coal contained in a firebrick chamber called a "gas-producer." A gas of this kind contains about one-third of its volume of carbon monoxide mixed with nitrogen from the air and a little carbon dioxide, etc. The ammonia is partly destroyed, but of late years a method introduced by the late Dr. Ludwig Mond has been very extensively adopted whereby a cheap coal slack can be used, at the

same time that nearly the whole of the nitrogen of the coal can be recovered in the form of ammonia. To secure this result the temperature must not be allowed to rise too high, and the yield of ammonia is augmented by driving into the coal a considerable quantity of steam. A portion of this is decomposed with formation of hydrogen gas and carbon monoxide, but the chief effect is to keep down the temperature. The increased collection of ammonia is attended by a considerable reduction in the value of the accompanying tar, which is quite different in character from the tar obtained at the gas works and from the coke ovens. The latter is produced at a much higher temperature, and its characteristic ingredients are hydrocarbons, which are related more or less closely to benzene (benzol) and its homologues. The tars produced at lower temperatures contain very little of these valuable compounds, their chief constituents resembling the oils obtained by moderate distillation of shales and consist chiefly of paraffins.

The Mond gas system has been adopted on a large scale in Staffordshire, a company having been formed a few years ago which generates the gas and supplies it through a system of mains to the surrounding district. Here it finds extensive employment in the gas engines which now assume such enormous dimensions, and in metallurgical furnaces as well as for raising steam and other purposes.

The tar obtained from gas works is black, heavier than water, and the amount produced per ton of coal varies considerably according to the character of the coal and the temperature to which it is heated. In ordinary gas works practice the distillation of the coal is so conducted as to yield 13,000 to 14,000 cubic feet of gas per ton of coal, and the tar amounts to 10–12 gallons, weighing a little more than 1 cwt. Roughly speaking then coal yields at about 1000° C., the usual carbonising temperature, approximately 5 per cent by weight of tar. When low-temperature carbonisation is employed, the temperature is then only about 600° C., and the yield of tar, which differs in composition from high-temperature tar, is about twice as great. The low-temperature process gives only 5000 cubic feet of gas per ton of coal, but it has a higher heating power, and leaves a smokeless fuel, known as semi-coke or "coalite," for which there is an increasing and welcome demand for domestic use.

From whatever source it is obtained, the distillation of coal-

tar forms a separate industry, some of the features of which, on account of its great practical and scientific importance, it is desirable to survey.

Before proceeding further, however, it will be interesting to glance at the following tables, which will give a rough idea of the enormous quantities of tar available and its connection with other valuable products.

The tendency is to save more and more of the by-products obtained by heating coal, and as the demand for the innumerable dyes, drugs, antiseptics, and other chemical compounds increases, so will the utilisation of the hydrocarbons from coal-tar continue to extend. In addition, these hydrocarbons, particularly "benzole," are in great demand, on account of their "anti-knock" properties, for admixture with petrol.

It is obvious, therefore, that there is every inducement to practise economy in the treatment of coal whether considered from the domestic or industrial point of view. The national importance of this economy has not as yet attracted the serious attention which it deserves, especially as far as the burning of raw coal in the domestic grate is concerned. About 40 million tons of coal is burnt each year in this manner in Great Britain, and quite apart from the serious wastage of by-products the smoke and dirt resulting contribute to the gloom of our large cities. In an address to the South Wales Institute of Engineers on January 17th, 1935, Mr. John Kane said "it had been estimated that in this country we poured out into the atmosphere each year the equivalent of 2 million tons of tar, half a million tons of motor spirit and nearly half a million tons of sulphate of ammonia, in addition to surplus gases." The use of smokeless fuel, obtained by low-temperature carbonisation in which by-products are saved, will no doubt become more widespread in the future, but at present it is merely touching the fringes of the problem.

The coal carbonisation industries, on the other hand, have made very marked progress during the present century in the direction of the abolition of the wasteful methods in use thirty years ago. In this connection the figures which will now be quoted show what has been achieved.

In an address to the Society of Chemical Industry in 1900, Dr. Beilby supplied the following figures, pointing out that if, at that time, beehive ovens had been entirely replaced by recovery

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ovens in the manufacture of blast-furnace coke the yield of tar, ammonia, and gas from this source would have been increased more than tenfold, since the proportion of beehives to recovery ovens was about 10 to 1.

PRODUCTS OF DISTILLATION OF COAL IN UNITED KINGDOM, 1899

Source.	Millions tons Coal distilled.	Millions tons Coke produced.	Tons Tar.	Tons Ammonium Sulphate.	Millions cubic feet of Gas.
Gas Works .	13	7-8	650,000	130,000	130,000
Blast Furnaces	2	—	150,000	18,000	360,000
Coke Ovens .	1 $\frac{1}{4}$	9/10	62,000	11,000	12,500
Totals .	—	—	862,000	159,000	—

A more recent estimate was made by Professor Bone in his address to the Chemical Section of the British Association at Manchester in September, 1915. From the following passage in this address we learn that the beehives formed only about 30 per cent of the coke ovens in the United Kingdom at that time.

“Of the 189 million tons of coal consumed in the United Kingdom in the year 1913, about 40 million tons, or (say) approximately one-fifth of the whole, were carbonised either in gas works, primarily for the manufacture of towns' gas, or in coke ovens for the manufacture of metallurgical coke—in practically equal proportions. Two-thirds of the latter was carbonised in by-product recovery plants; the remainder in the old wasteful beehive ovens. So that, roughly speaking, we have :

Total Coal Carbonised=40 Million Tons.		
In Gas Works.	In By-Product Coke Ovens.	In Beehive Coke Ovens.
20	13·5	6·5

“At present there are 8297 by-product coke ovens built in this country, of which 6678 are fitted with benzol recovery arrangements, capable of producing something like 10 million tons of coke per annum.

“The yields of the various by-products obtainable on such coke oven installations naturally vary with the locality and character of the coal seam; but they probably average some-

what as follows—expressed as percentages on dry coal carbonised :

District.	Ammonium Sulphate.	Tar.	Benzol and Toluol as Finished Products.
Durham . . .	0.9 to 1.45	2.5 to 4.5	0.6 to 1.0
Yorkshire . . .	1.3 to 1.5	3.5 to 5.0	0.9 to 1.1
Derbyshire . . .	1.3 to 1.6	3.5 to 5.0	0.9 to 1.1
Scotland . . .	1.4 to 1.6	3.5 to 5.0	0.9 to 1.1
South Wales . . .	0.9 to 1.1	2.0 to 3.5	0.6 to 0.75

Or, to put the matter a little differently, each ton of dry coal carbonised yields from 20 to 35 lbs. of ammonium sulphate, from 56 to 112 lbs. of tar, and from 2 to 3½ gallons of crude benzol, etc., according to the locality. About 65 to 70 per cent of the crude benzol is obtained as finished products—benzene, toluene, solvent and heavy naphthas.

“How rapid has been the development of the by-product coking industry in this country during recent years may be judged from the following official returns of the quantities of ammonium sulphate annually made by such plants, as compared with the corresponding quantities produced in gas works.

TONS OF AMMONIUM SULPHATE PRODUCED IN

Year.	By-Product Coke-Oven Plants.	Gas Works.
1903 . . .	17,435 ..	149,489
1908 . . .	64,227 ..	165,218
1913 . . .	133,816 ...	182,180

“In the natural course of events the final disappearance of the wasteful beehive coking oven from this country is now only a matter of a few years.”

This forecast of Professor Bone, made twenty years ago, appears to be nearing realisation, as is shown by the following figures for coking ovens in Great Britain :

Year.	Beehive Ovens.	By-product Ovens.
1908 . . .	19,478 ..	6737
1913 . . .	13,167 ..	9839
1929 . . .	1,401 ..	8138

In spite of the very large decrease in the number of beehive ovens, the amount of coke produced, between 12,000,000 and 13,000,000 tons per annum, has remained almost unchanged since 1913; the increased capacity of the by-product ovens accounts for the maintenance of output in spite of the decrease in their number, and the almost complete elimination of beehive ovens. It is estimated that only 4 per cent of the total coke produced in Great Britain, and 6 per cent of that in the United States, is now made in beehive ovens. Attention may be called to the fact that during 1930 the production of ammonium sulphate was 173,000 tons from by-product ovens and 125,000 tons from gas works; the decrease in the latter, as compared with the figures in Professor Bone's address, is attributed to the low price now obtained for ammonium sulphate on account of the serious competition of the synthetic product (chapter XXVII).

Now resuming the subject of this chapter, which is Coal-Tar, we may estimate the amount produced by all the countries of the world. Actual data are difficult to obtain, but an idea may be obtained from the facts that about 70 million tons of coal are used annually in gas works, and about 110 million tons in by-product coking plants; assuming that 5 per cent of the coal is recovered as tar this gives a total of approximately 9 million tons of tar available annually. This may be compared with the estimate of 2,660,000 tons of tar for the year 1901. Not all the tar obtained is worked up for by-products, described below, but considerable quantities are used for road-making; in Great Britain, for example, about two-thirds of the $1\frac{1}{2}$ million tons of tar is distilled to obtain benzol, carbolic acid, etc.

Coal-tar is often distilled in large iron stills set in brickwork and heated by a fire below. Each still is a sort of cylindrical boiler which holds from 20 to 45 tons. In England the cylinders are vertical, holding generally about 20 tons of tar, but in America horizontal cylindrical stills, with a capacity of about 45 tons, are in common use. The still is fitted with a pipe by which the vapour is carried into a spiral continuation of the same called a condenser and in which it is liquefied. The condensed product runs into different receivers. First come some ammoniacal liquor and the light oils which float on water. These are followed, as the temperature rises, by heavy oils which sink in water. The residue left in the still is pitch, which while still hot is run out into large iron vessels where it cools and gradually becomes

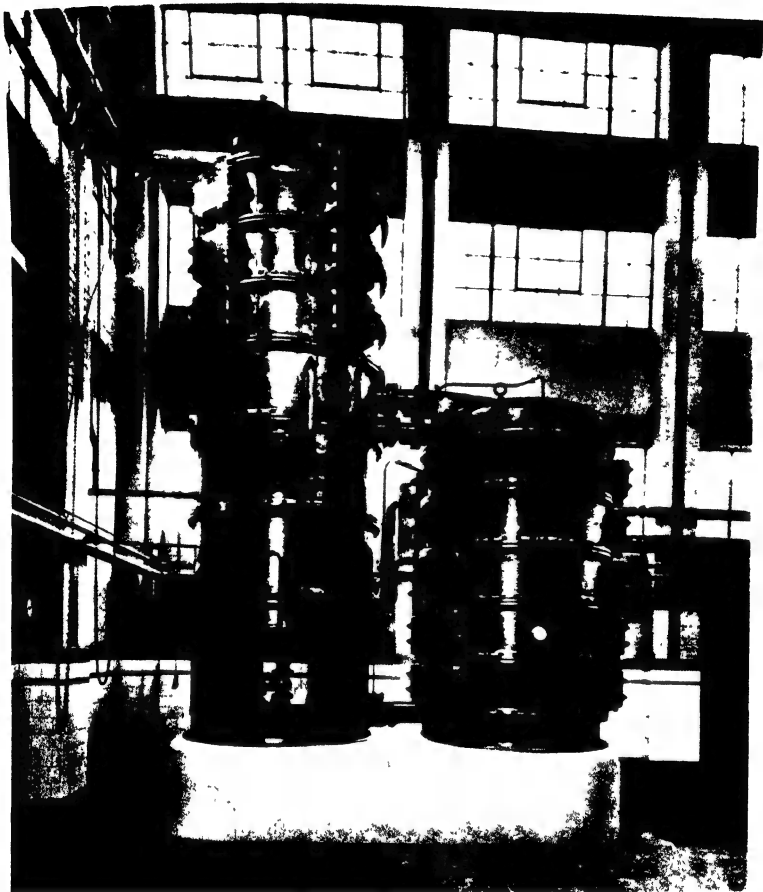


FIG. 88 —AMMONIA STILL, BY-PRODUCT RECOVERY PLANT, NORMANBY
WORKS, SCUNTHORPE

(By courtesy of The Woodhall-Duckham Co., Ltd.)

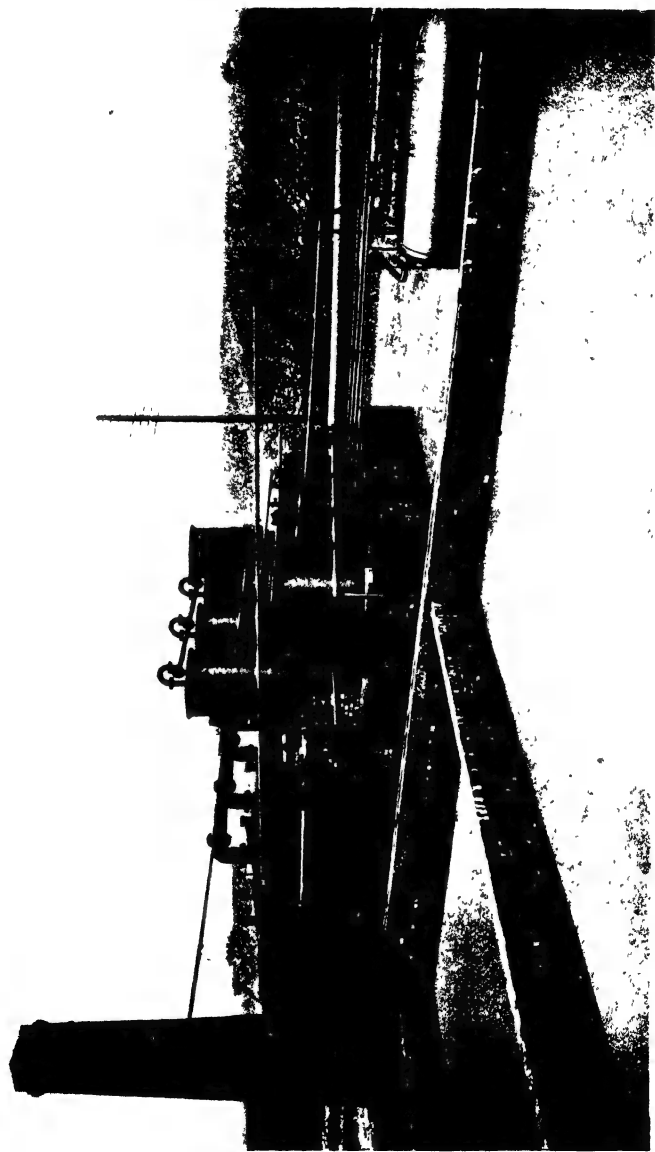


FIG. 89.—HIRD'S CONTINUOUS TAR DISTILLATION PLANT

solid. Ordinary gas works tar is an exceedingly complex mixture of upwards of two hundred different chemical compounds. These may be divided into hydrocarbons, of which the most important are benzene, toluene, xylene, naphthalene, anthracene, etc., and compounds containing oxygen, of which the most important are phenol, commonly called carbolic acid, and other substances of that class. A small proportion of basic substances containing nitrogen, and others containing sulphur are also present, but are of minor importance and at this point may be neglected.

The composition of the tar obtained by low temperature distillation is somewhat different, and although there is relatively little of this material yet available it is very likely to grow in importance. It contains almost none of the hydrocarbons of high-temperature tar, but instead it has hydrocarbons of the paraffin and cyclo-paraffin type, which are useful as motor-fuel; the proportion of carbolic acid and related substances is also much higher than in high-temperature tar.

On distillation 1 ton of average gas works tar will produce approximately :

Ammoniacal Liquor	5 gallons
Crude Naphtha	5·6 „
Light Oils	26·0 „
Creosote Oils	17·0 „
Anthracene Oils	38·0 „
Pitch	12 cwt.

The value of the products from coal-tar has led to the invention of many modifications in the form of the stills and in methods of distillation; one of the most important of these is the development of continuous processes, three of which will be described here. In the process of Messrs. Hird, Chambers, and Hammond, of Huddersfield, which has been used in England although it does not seem to have been very successful in America, a series of stills at different temperatures are used. The crude tar flows into the one at the lowest temperature, where it gives off its most volatile constituents, which may be passed into a condenser and collected. The residue in the still then flows into a second still alongside of the first, and being heated to a higher temperature the portion distilling away consists of liquids having a higher boiling-point. Similarly a third still may be arranged so

as to receive the residue from the second as it parts with its vaporisable constituents. A series of three stills is found to be sufficient, and the final residue runs into the pitch-cooler. The process is made continuous by placing the crude tar tank at a higher level than the stills so that the tar flows through them under the influence of gravity.

The picture Fig. 89 provides a view of this continuous plant in operation.

Another form of continuous still, which appears to be much used in the United States, and has been worked successfully for some time in England, is somewhat similar in principle to the pipe-stills used for continuous petroleum distillation. The tar is kept flowing through a coil immersed in a furnace, and the vapour coming off passes through a number, generally three, of condensers at different temperatures; in the first of these the anthracene oil is condensed, in the second the creosote oil, and in the last and coolest the light oil condenses. It is claimed that as the tar is heated for a short time only, whilst flowing through the coil, there is less decomposition and a higher yield of oils results. A continuous pipe-still of large capacity is capable of dealing with as much as 25,000 gallons, that is about 130 tons, of tar in a day. The photograph in Fig. 90 shows a Wilton's Patent tar-still; the furnace is seen at the right, and the tall column acts as a heat exchanger for warming up the incoming tar, some low boiling-point constituents being removed at the same time.

An important new type of continuous still, which is attracting much interest, is the T.I.C. plant of the Woodhall-Duckham Co., London; the tar, after dehydration and removal of ammonia, flows continuously on to the surface of a molten metal alloy, kept at the appropriate temperature, in a flat circular still, the largest being 7 feet in diameter and having a maximum depth of 14 inches. The vaporisable matter passes off immediately from the tar and is condensed in a series of columns kept at different temperatures; in the hottest the anthracene condenses, then comes the heavy creosote, followed by the light creosote and finally the crude naphtha is condensed out in special coolers. The pitch remaining in the still flows away continuously from the surface of the alloy. The largest single still of this type can deal with about 8000 gallons of tar in twenty-four hours, but at no time is there more than ten gallons in the still, where it forms

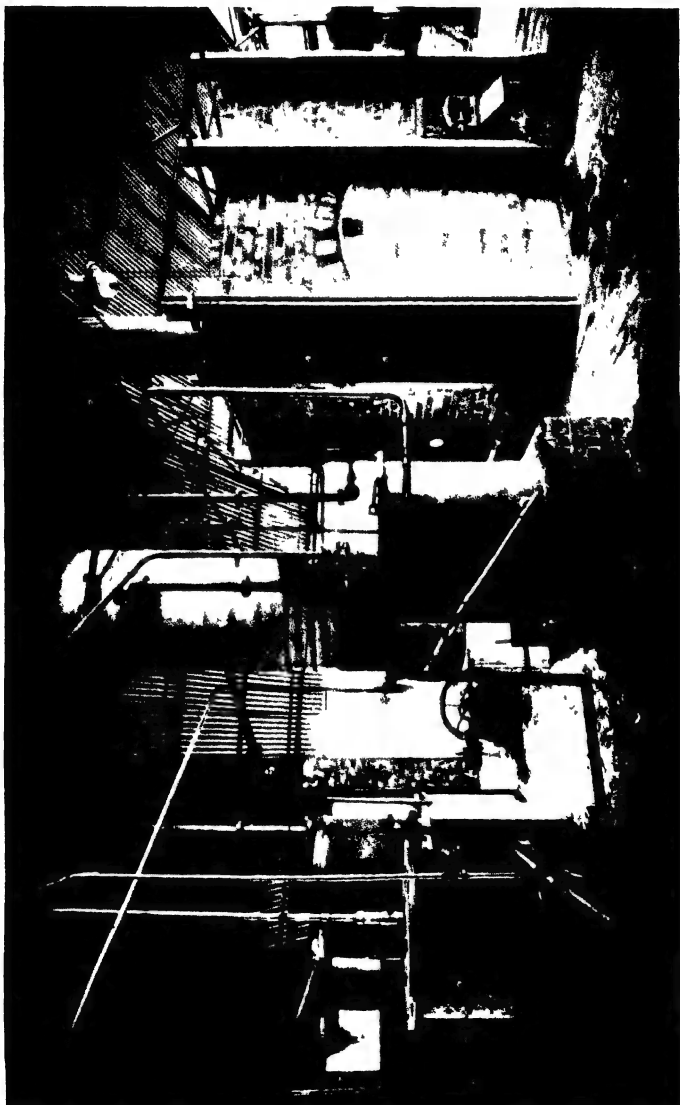


FIG. 90 WILTON CONTINUOUS TAR STILL, AT WELLINGBOROUGH GAS WORKS

(By courtesy of *The Chemical Engineering and Wilton's Patent Furnace Co., Ltd.*)

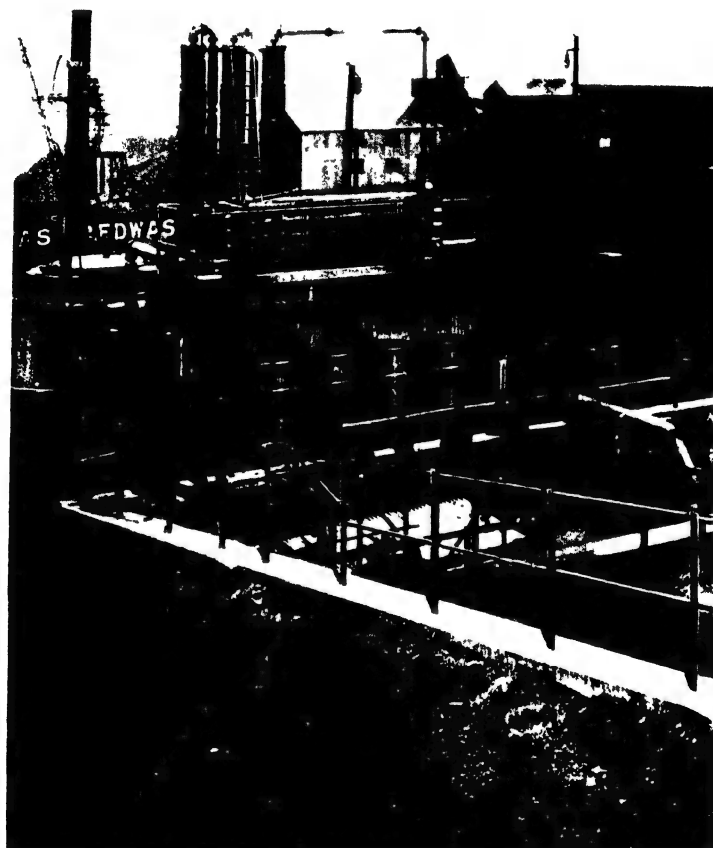


FIG 91 --T I C TAR-DISTILLATION PLANT, BEDWAS, SOUTH WALES

(By courtesy of *The Woodhall-Druckham Co., Ltd.*)

a film less than one-eighth of an inch in thickness on the surface of the hot alloy. The danger of fire and of decomposition due to super-heating is thus avoided. The photograph in Fig. 91 shows the compact nature of a T.I.C. plant of 6000 gallons daily capacity; the still itself, at the extreme left, three condensing columns and a number of tanks for receiving various condensates are clearly seen.

We may now proceed to consider the next step, which consists in dealing with the several products of the distillation in the tar stills. The ammoniacal liquor goes to a different department where it yields sulphate of ammonia. The crude naphtha and light oils are usually redistilled for the separation of benzene¹ and its homologues. But as it contains small quantities of basic substances, including aniline, it is first shaken up with sulphuric acid which removes these compounds, and subsequently with caustic soda which separates any carboic acid and the residual sulphuric acid. After washing with water, the hydrocarbons boiling between 80° and 150° C. are transferred to the naphtha still.

The capacity of the still is about 5000 gallons, and it is heated by steam. Its purpose is to separate from impure benzol or naphtha the pure hydrocarbon benzene. In order to do this it is necessary to provide for the condensation, from the vapour which passes up the fractionating column, of those constituents toluene (b.p. 110° C.), the xylenes (b.p. 137° to 142° C.), and other hydrocarbons present in the crude benzol which boil at temperatures above the boiling-point of benzene (b.p. 80·5° C.). With this object the column itself is divided by horizontal plates, in each of which are placed a number of valves opening upwards, and a tube open at top and bottom and projecting an inch or so above the plate. The latter is thus kept covered with a layer of liquid through which the vapour bubbles in its passage upward. The vapour of the pure benzene then passes into the coil surrounded by cold water and is thus delivered in the form of liquid into the receiver. Benzene of any lower degree of purity can be obtained by simply cutting off the connection between the cooler and the pipes leading back to the column.

With regard to the remaining fractions of the tar distillates it will be sufficient to follow the course of three of them.

¹ These hydrocarbons are called commercially benzol, toluol, etc., but the pure hydrocarbons are in chemical language distinguished as *benzene*, *toluene*, etc.

Naphthalene is a white crystalline solid which melts at 79°C . and boils at 218°C . It is contained in the light oils and in the creosote oils. When the latter are stirred up with caustic soda the carbolic and cresylic acids (phenol and cresol) present are dissolved out, and on standing the watery liquid separates from the undissolved oil which contains much naphthalene. The tar acids are separated from the caustic soda solution by heating the liquid in the presence of waste carbonic acid gas, and by further treatment pure *phenol* is obtained.

Anthracene is a crystalline solid which when pure exhibits a beautiful blue fluorescence. It melts at 213°C ., and boils at 351°C . Anthracene separates on standing from the crude oil in the form of a greenish crystalline solid which is filtered off, pressed, and washed free from oil by the use of a little solvent naphtha.

Creosote oil, which is the residuum left after treatment in the manner indicated above, is used on a very large scale as a preservative for timber.

Crude coal-tar finds some applications without being separated by distillation into its components. These are familiar enough. But as the starting-point for chemical industry it may be worth while to summarise the chief applications which are made of the chemical compounds isolated from coal-tar. These are given in the following table :

	Crude.	Pure.
Benzene	Motor fuel, Solvent.	Dyes.
Toluene	Solvent.	Dyes. Explosive T.N.T.
Xylenes	Solvent Naphtha.	Dyes.
Naphthalene	Insecticide and Mild Antiseptic.	Dyes.
Phenol	Strong Antiseptic and Disinfectant.	Dyes. Explosive. Artificial resin.
Anthracene		Dyes.

Before going on to deal with the products of coal-tar distillation mention may be made here of the important process of hydrogenation of coal and tar-oils for the production of motor spirit. The original idea was suggested by the German engineer Bergius in 1914, but it has taken nearly twenty years to make the process a commercial success. The hydrogenation is carried out in two

stages which are really independent of one another : these are the "liquid phase" and "vapour phase" stages, respectively. For the liquid phase process finely powdered coal is made into a paste with tar or with heavy (creosote) oil from tar distillation ; this is heated to about 450° C. and hydrogen gas is passed in at 250 atmospheres (3700 lbs.) pressure in the presence of a catalyst able to resist the action of sulphur. A very large number of substances have been patented for use as catalysts, and probably their true nature is kept secret, but Dr. Pier, the German authority on the subject, mentions molybdenum and tungsten sulphides. After suitable time the hydrogenated mass is distilled : the light fraction, constituting about 30 per cent of the original coal, is refined and used as motor spirit ; the middle fraction (37 per cent) passes on to the vapour phase converter, and the heavy oil is used for further mixing with coal.

The vapour phase process uses either creosote oil, especially from the low temperature distillation of coal, or the middle fraction from the liquid phase process : the oils are vaporised at a temperature of 400° to 500° and passed together with hydrogen under high pressure over a catalyst. When cooled and distilled the product gives 80 to 90 per cent of motor spirit, so that there is a net yield of over 60 gallons of spirit per ton of coal consumed in the hydrogenation process ; in addition there is an equal amount of coal used for steam raising, producing hydrogen, etc., so that it requires 3.65 tons of coal to give 1 ton of "petrol."

In Germany both liquid and vapour phase processes of hydrogenation were in operation in 1935, and it is estimated that during that year about 300,000 tons of motor spirit will be produced ; the plant is designed for an annual output of 500,000 tons. The Imperial Chemical Industries Ltd. have erected a hydrogenation plant at their Billingham works which should be capable of producing at least 150,000 tons of motor spirit per annum ; in the early part of 1935 the first shipment of spirit, obtained by the vapour phase hydrogenation of creosote oils from coal-tar, was made, and the liquid phase process was expected to be in operation shortly afterwards.

CHAPTER XXI

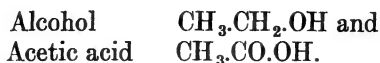
PRODUCTION OF DYES

It is perhaps scarcely necessary to state the fact that coal-tar does not contain ready-formed anything in the nature of a dye, nor anything which possesses colour, except of course the black highly carbonaceous substances which are left after distillation. But that such an idea still lurks in the minds of some people is indicated by the legend formerly current, that Perkin, the discoverer of mauve, the first of these artificial colouring matters, was attracted to the subject by noticing the beautiful tints displayed by a film of tar floating on water. Such colours are, of course, due to the thinness of the film, and have nothing whatever to do with its composition.

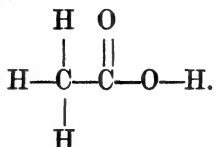
In order to render intelligible the chemical changes which are involved in the successive stages of the production of the numerous synthetic dyes, drugs, perfumes, and other so-called organic compounds, a very brief statement of the meaning of chemical symbols is necessary. How they are arrived at, and the full extent of their meaning, are questions which are beyond the scope of this work, but can be answered by reference to the textbooks of chemistry.

A chemical symbol such as C or H is usually the initial letter of the name of an element, carbon or hydrogen for example. It is used to signify one *atom* of the element, and when two such symbols stand side by side, the elements are represented in combination, thus H_2O means that two atoms of the element hydrogen are combined with one atom of the element oxygen, forming one *molecule* of the compound, water. The symbols are also used for the purpose of displaying what is believed to be the order in which the elements in a compound are joined together. Thus the formula for water, H_2O , may be written H.O.H or H-O-H, by which expressions the idea is conveyed that the atoms united together in a molecule of water are not jumbled together irregularly, but that each atom of hydrogen is attached to the oxygen and is unconnected, at least directly, with the other atom of hydrogen. Similarly any number of atoms of

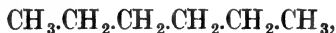
carbon may be joined together, and at the same time combined with hydrogen or other elements as in the formulæ for



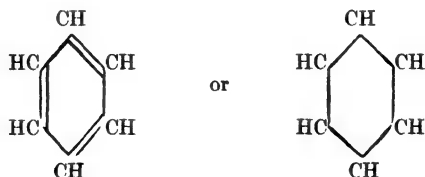
Such expressions may be expanded if necessary so as to show the manner in which each atom is joined to the others as in the case of acetic acid :



Further there are reasons for believing that a number of carbon atoms joined together do not really range themselves in straight rows as it is convenient to write them on paper, for instance,



but that there is often a tendency to the formation of closed chains or rings as in the case of benzene, C_6H_6 , which is represented by the formula below :



In this case the expression is required so frequently in writing the formula for organic compounds that it is customary to reduce it to the skeleton thus :



which is generally understood without writing the symbols for the several atoms.

The first synthetic dye was produced accidentally by W. H.

Perkin¹ in 1856 when engaged in a research having a different object in view. The product was called *mauve* from the colour which resembles that of the flower of the mallow (French=*mauve*), and although it has long ceased to be manufactured as a dye for silk and wool, owing to its tendency to fade in sunlight, it has been used in more recent times for colouring postage stamps.

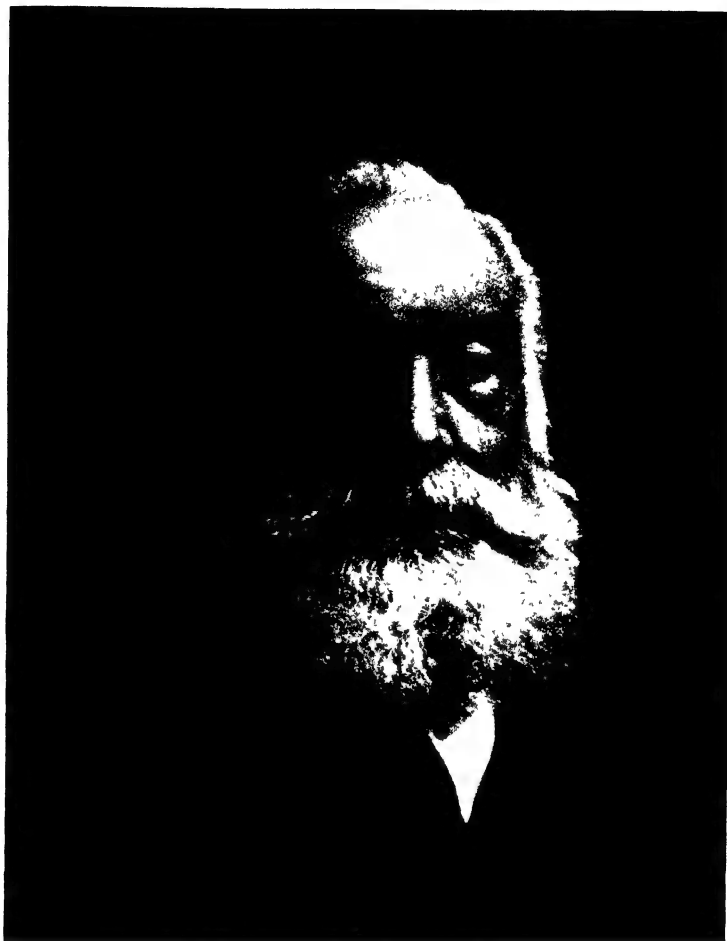
Mauve was produced by adding potassium dichromate to a solution of aniline in dilute sulphuric acid, whereby a black precipitate was formed, which after removal of impurities by boiling it in coal-tar naphtha, was dissolved in alcohol in which it forms a rich purple-coloured solution.

Dichromate of potassium is an oxidising agent, and naturally other oxidising agents were tried as soon as the process became known. This led to the discovery of the red dye magenta. Strangely enough pure aniline acted upon by these oxidising

¹ William Henry Perkin was born in London, on March 12th, 1838, the youngest son of G. F. Perkin, a builder and contractor. After a few years at the City of London School he entered the Royal College of Chemistry in 1853, where his progress was so rapid that he soon commenced research. In 1856, whilst attempting to produce quinine synthetically, he submitted to oxidation a specimen of commercial aniline containing variable proportions of the toluidines; the result was a dark coloured product from which, after further experiments, the famous "mauve" dye was obtained. This discovery was exploited in a factory built at Greenford Green, Middlesex. In spite of his entry into chemical industry Perkin was devoted to research in its purely scientific interests, and discovered a general method, usually known as "Perkin's reaction," by means of which he prepared coumarin and cinnamic acid. In 1874 he retired from business as a manufacturer, and devoted himself to scientific research, mainly a study of magnetic rotatory power, in his private laboratory at Sudbury. Perkin was elected to the Fellowship of the Royal Society in 1866, and he held the Presidency of the Chemical Society, the Society of Chemical Industry, and the Society of Dyers and Colourists. He died on July 14th, 1907.

Perkin's eldest son, W. H. Perkin, Jr., was born at Sudbury on June 17th, 1860, and like his father he studied at the City of London School and the Royal College of Chemistry. After spending two years, 1880 to 1882, as a research student at Wurzburg, and four years at Munich, he was appointed in 1887 as the first Professor of Chemistry at the Heriot-Watt College, Edinburgh. In 1892 Perkin went to Owen's College, later the University, Manchester, and in 1913 he was elected as Waynflete Professor of Chemistry in the University of Oxford; this post he was still holding when he died on September 17th, 1929. Perkin carried out a very large amount of important synthetical work dealing with camphor, terpenes, alkaloids and other groups of compounds, and he also supervised the research work carried out during the war and afterwards in connection with the development of the new British dyestuff industry. Perkin was awarded the Longstaff Medal of the Chemical Society in 1900, and he received the Davy Medal (1904) and Royal Medal (1925) of the Royal Society.

Two other sons of W. H. Perkin, Senior, namely, Arthur George and Frederick Mollwo Perkin, have also achieved fame as chemists.



Yours sincerely
W. W. Perkin

agents does not yield a dye, but fortunately the benzene of former days was very far from pure, and contained a varying quantity of toluene, the hydrocarbon which stands next to benzene in the series and possesses very similar properties. These hydrocarbons, which are extracted by distillation from coal-tar, form the starting-point for the production of this class of colours. The successive steps in the production of magenta are the following.

Benzene acted upon by strong nitric acid is converted into nitrobenzene, $C_6H_5NO_2$. Toluene, C_7H_8 , is similarly converted into nitrotoluene, $C_7H_7NO_2$, or rather into a mixture of two compounds having the same ultimate composition, though differing in the arrangement of the constituent atoms.

When nitrobenzene is brought into contact with a substance or mixture of substances, such as iron and acetic acid, which is capable of supplying hydrogen, the two atoms of oxygen are removed and two atoms of hydrogen are introduced in place of them, and aniline, $C_6H_5NH_2$, is the result. The nitrotoluenes, under the same circumstances, are affected in a similar manner, and give rise to bases called toluidines, $C_7H_7NH_2$.

Now as the commercial benzene seventy years ago consisted of a mixture of benzene and toluene, the aniline which resulted from using it as the parent material always consisted of a mixture of aniline and ortho- and para-toluidines. Such a mixture acted on by an oxidising agent yields a deep red mass which contains a magenta dye.

The apparatus employed in these operations is simple in principle. The nitration of benzene or toluene is effected by bringing the hydrocarbon into contact with the requisite quantity of a mixture of strong sulphuric and nitric acids, the former being employed to combine with the water generated in the reaction.

The mixture is made in a cast-iron pot, cooled externally by water, and provided with a paddle. A number of these vessels stand side by side, and the contents are stirred by power. After the action of the acid is completed the nitrobenzene or nitrotoluene floating on the acid is separated, and is washed free from acid by mixing it with water in a similar iron or glazed stoneware vessel. It is then separated from the water in which it sinks. Nitrobenzene is a pale yellow liquid with a strong smell of bitter almond oil, and is to some extent used in perfumery under the name of "Oil of Mirbane."

The conversion of nitrobenzene into aniline is effected in a series of vessels, the arrangement of which is shown diagrammatically in the figure.

a is a cast-iron pot provided with a stirrer *c*, the axis of which *b* is a pipe by which steam may be introduced when required.

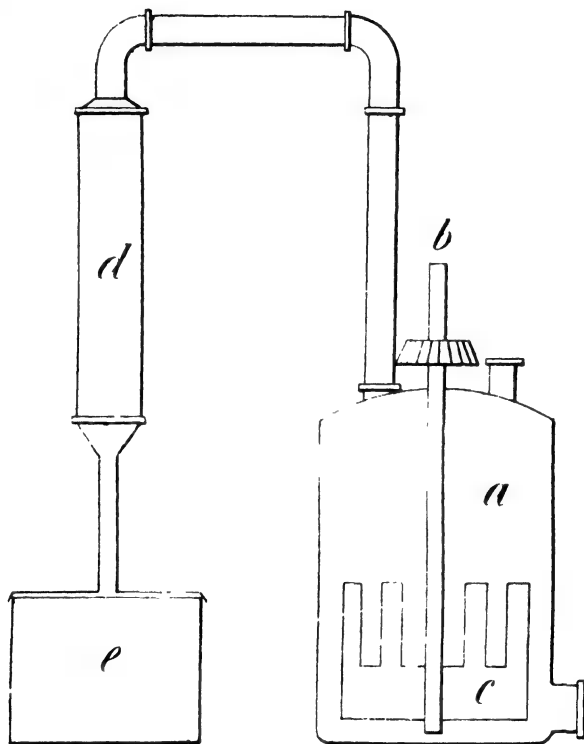


FIG. 92. ANILINE STILL.

Nitrobenzene and a little hydrochloric acid are placed in the pot, and iron borings are added to the mixture, which is kept warm by steam and stirred by the paddle till the reaction commences. Once started the chemical action, which is attended by the evolution of heat, proceeds till the reduction of the nitrobenzene is complete. At this stage any aniline evaporating from the mass condenses in the upright pipe and returns to the reduction vessel. Lime is then added to neutralise the acid,

and the aniline distilled off through the condenser *d* into the receptacle *e*.

Aniline is a colourless liquid which boils at $182-3^{\circ}$ C., and becomes brown by exposure to air. It sinks in water but slowly, as its specific gravity is only 1.024 at 16° . It is slightly soluble in cold water.

The toluidines are produced in a similar way from toluene, and, as already explained, the red magenta is formed by oxidising a mixture of these bases. Several oxidising agents have been and are still used. Of these arsenic acid is one of the most convenient, but the use of this reagent involves the careful removal of arsenic from the finished colouring matter. The presence of even a small quantity of arsenate or arsenite in the dye applied to fabrics which are used for any kind of clothing which comes into direct contact with the skin, leads to irritation of the surface, and even to symptoms of arsenical poisoning.

Another process for making aniline red or magenta avoids the use of arsenic and yields a somewhat larger quantity of the colouring matter. In this method the aniline and toluidine are first converted into their solid salts by dissolving in hydrochloric acid and drying. To this mixture is then added a further quantity of the aniline oil together with nitrobenzene, which is the source of the oxygen required, and the whole is heated till the temperature reaches about 190° C., when a small amount of iron borings are added. The action is complicated. Oxidation by nitrobenzene has almost displaced the use of arsenic acid, but the latter is said to be still employed in making magenta in relatively large crystals for export.

Magenta is a compound in which a base, called *rosaniline*, is united with an acid. The product of the operations just described is rosaniline hydrochloride, but in fact the rosaniline produced consists of a mixture of two compounds, one of which, $C_{19}H_{17}N_3HCl$, is called *pararosaniline*, while the rosaniline is a homologous compound containing $C_{20}H_{19}N_3HCl$. These are both red colouring matters which dye silk and wool direct, and both are present together in the common dye.

Strangely enough the rosanilines alone are quite colourless compounds and only form dyes when united with an acid, in the proportions indicated in the formulæ already given. Both these bases are capable of combining with three molecules of hydrochloric acid altogether, forming yellowish brown

crystallisable compounds, but these again are not colouring matters.

Magenta is easily soluble in water, forming a magnificent red liquid from which large crystals, having the appearance of green beetle wings, may be obtained by slow deposition.

The use and appearance of substances of this kind have become so familiar that few people of the present generation can imagine the excitement and interest aroused when large frames covered with jewel-like crystals of these dyes were shown in the International Exhibition of 1862 in London. The crowds attracted to the showcases containing these objects were as great as those which gathered round the Koh-i-noor in 1851.

If we refer to Hofmann's interesting Report on the Chemical Products and Processes in the Exhibition of 1862 a few facts may be extracted which serve to show how strangely the condition and distribution of the industry relating to colours from coal-tar have changed in the seventy years which have elapsed since that time. In the first place the reporter enumerates the chief colours then recently discovered. These are practically all included under the several headings of paragraphs in the Report, viz. : Aniline Violets (mauve), Aniline Red (magenta), Aniline Yellow (chrysaniline), Aniline Blue, Quinoline Blue, Colouring Matters derived from Phenol (rosolic acid and picric acid), with a short paragraph relating to early results obtained with derivatives of naphthalene. Where one artificial substance capable of employment as a dye was known in 1862, there are probably a hundred now available ; in fact about two thousand artificial dye stuffs are known at the present time, most of which are in actual use for dyeing purposes. It is also important to notice who were the manufacturers of colours from coal-tar at the time of the exhibition. This can be gathered from the number of awards and medals and honourable mentions to the chief European countries represented. The United Kingdom received twelve medals and four honourable mentions, France received twenty-one medals and five honourable mentions, Germany and Austria together obtained twelve medals and seven honourable mentions. Speaking of aniline red the reporter, a German, makes the following statement :

" Amongst those who have succeeded best are, in France, Messrs. Renard Brothers and Franc and Messrs. Fayolle and Co., lciencees of Messrs. Renard of Lyons, who have exhibited aniline

reds, violets, and blues of great beauty, and to whom a just tribute of eulogium has been given.

"In Germany M. R. Knosp of Stuttgart, and in Switzerland Messrs. J. J. Müller and Co. of Basle have also acquired a well-merited reputation.

"But it is in England that the most beautiful products have been obtained; in proof of which assertion the reporter confidently points to the splendid exhibition of Messrs. Simpson, Maule, and Nicholson which has attracted such general attention. It is only justice to state that while France has had the merit of inaugurating the industrial production of aniline red, England, may, thanks to the activity, science, and untiring efforts of Mr. Nicholson, claim the honour of having brought this manufacture to its present high degree of perfection."

It may well be asked why and when did England decline from this high position? The answer has been given repeatedly since 1880, when Germany had already succeeded in carrying off a large part of the business of manufacturing colours from coal-tar from England to the Continent. In the repeated warnings which have been issued since that time in no uncertain voice by Meldola, Green, the Perkins (father and son), and many other English chemists, two causes for the change have invariably been indicated: first the neglect of organic chemistry in the universities and colleges of this country, and then the disregard by manufacturers of scientific methods and assistance and total indifference to the practice of research in connection with their processes and products. As to the former no such charge can now be brought against the chemical schools of this country. Manufacturers have also been aroused and the steps which have been taken both by them and by the Government since the war have had the effect of re-establishing the dye industry in Great Britain. The following figures show the quantities of dyestuffs produced in the United Kingdom in 1913, for purposes of comparison with those of more recent years.

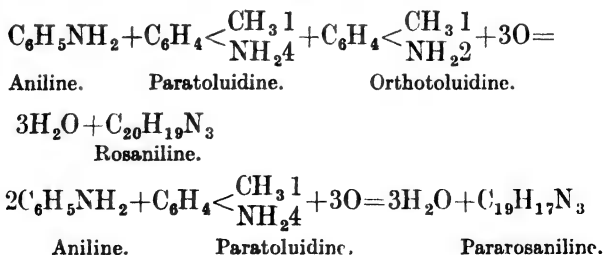
DYESTUFF PRODUCTION IN GREAT BRITAIN

Year.	Weight in Pounds.
1913	9,114,134
1922	23,832,967
1926	30,297,000
1930	42,590,243
1933	52,944,866

In 1913 over forty million pounds weight of dyestuffs were imported, but in the past few years the amount, as is to be expected from the figures quoted, has dropped to about five million pounds per annum.

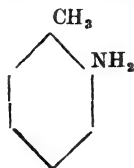
Several other countries have shown an increase in the production of dyestuffs since the war, but in the United States this has been most spectacular; the extent of production was only 6,500,000 lbs. in 1913, but it had risen to about 100,000,000 lbs. in 1933. In Germany there has been a corresponding fall from 290 millions to 100,000,000 lbs. in 1933.

It will be evident that not only are dyes not present in coal-tar ready formed, but that the hydrocarbons which are present in coal-tar and are got out of it, as already explained, by distillation, are converted into the colouring matter by undergoing successive chemical changes whereby several intermediate products are formed. The intermediate compounds if merely mixed together would not produce a dye, but when acted upon by chemical agents each one loses a portion of one of its constituents, the hydrogen for instance, and receives something in place of it, and a new compound or association of atoms is formed which has properties different from the properties of the separate materials concerned. Thus a molecule of aniline, $C_6H_5NH_2$, one of orthotoluidine, $C_7H_7NH_2$, and one of paratoluidine, $C_7H_7NH_2$, when attacked by three atoms of oxygen jointly lose six atoms of hydrogen, while the three altered residues combine to form rosaniline. Pararosaniline is produced in like manner when a mixture of aniline and paratoluidine is attacked by oxygen. Equations representing these changes may be written as follows :



The prefixes *ortho* and *para* and the numerals 1 : 2 and 1 : 4 introduced into the formulæ refer to the relative positions in the molecule of the constituents methyl, CH_3 , and amino, NH_2 .

The constitutional formulæ of ortho- and para-toluidines would be represented by the following diagrams, the meaning of which has been already explained :

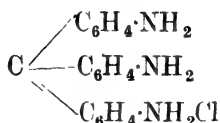


Orthotoluidine.

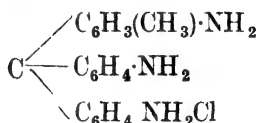


Paratoluidine.

The colouring matters are each built up of three groups of this kind held together by an atom of carbon. They are represented by the following expressions in which every group of C_6 must be regarded as forming a ring or closed chain of carbon atoms.

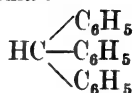


Pararosaniline hydrochloride.



Rosaniline hydrochloride.

There are a number of other colouring matters constructed on the same type ; they are all derivable from one parent hydrocarbon called triphenylmethane, the composition of which is represented by the formula :



Such a substance has no colour and cannot act as a dye. Nevertheless the introduction of certain other constituents, such as NH_2 , etc., results in many cases in the formation of the highly coloured compounds, such as magenta. It is obvious, therefore, that the production of a dyestuff depends not so much on the elements which are present, as the order in which they are united together, in other words on the *constitution* of the molecule. An immense amount of research and of speculation has been expended on the endeavour to find general rules which explain the tinctorial property. Here we must learn to distinguish from true dyes substances which exhibit colour, but

which are incapable of attaching themselves to fibre, and therefore are not dyes. Thus, for example, azobenzene, $C_6H_5N=NC_6H_5$, is a red substance but it has no dyeing properties. But a compound having a similar constitution, so far as the two nitrogen atoms are concerned, is diamino-azobenzene,



which, in the form of hydrochloride, forms the orange dye called *chrysoidine*.

Groups of atoms, such as $-N=N-$, are called *chromophors*, as they have the property of producing a dye when introduced into certain compounds called *chromogens*. The theory is still a subject of debate, as from time to time examples occur which seem not to comply with the rule. The whole subject is, however, too complex and technical for treatment in these pages.

It would not be possible in the space at our disposal to describe the production of more than a few representative colours. Among these indigo stands in a remarkable position owing to the efforts which have been made during many years to replace the natural by the artificial synthetic product. These efforts have within recent years been crowned with such commercial success that the production of natural indigo has sunk to insignificant proportions.

Indigo is a blue substance, insoluble in water, which has long been obtained from the juice of various species of *Indigofera* (Nat. Ord. *Leguminosæ*), cultivated for this purpose in the East. That its use as a dye has been familiar for ages is indicated by the fact that the blue cloths found on Egyptian mummies owe their colour to this substance. Its introduction into Europe from India appears to have occurred in the seventeenth century. The only European plant which yields indigo blue is the woad (*Isatis tinctoria*, Nat. Ord. *Cruciferae*), which was formerly cultivated to a considerable extent in the eastern counties of England. Its use has much declined of late years, though until 1932 a small quantity was grown in Lincolnshire for addition to artificial indigo dyeing baths.

The indigo plant is herbaceous and grows to a height of about 3 feet. The seed is sown in spring or autumn according to variety and the nature of the soil. The plant is cut just before flowering and is made into bundles which are placed in tanks or steeping



FIG 93--INDIGO PLANT STAGES OF GROWTH

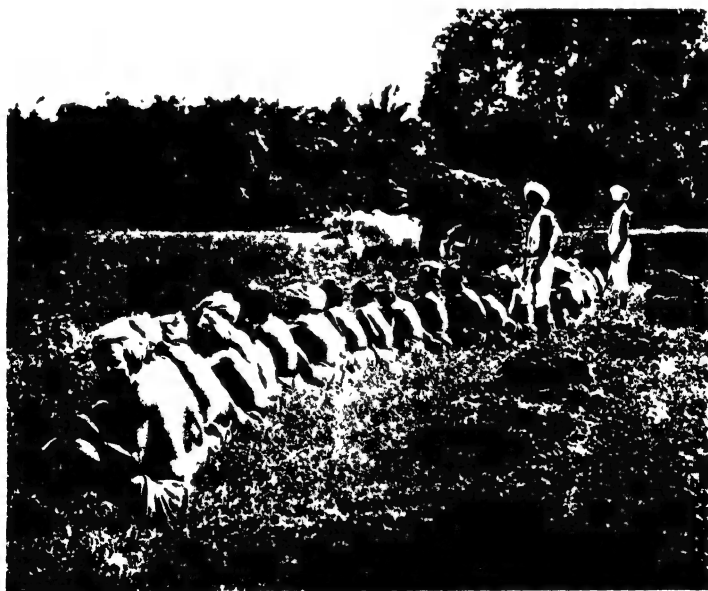


FIG 94--INDIGO CUTTING THE PLANT

vats. The herb is then covered with boards, weighted with stones, and water is added sufficient to cover it. A peculiar fermentation ensues, which lasts from twelve to fifteen hours according to the temperature of the air. From time to time a small quantity of the liquid is taken from the bottom of the vat and when it exhibits the desired yellow colour the liquor is run off into a separate tank, where it is agitated either by a paddle-wheel or by workmen who stand in the liquid and beat it with paddles.

In this process oxygen is absorbed from the air and indigo appears as a greenish blue precipitate. This is allowed to settle and is then boiled with water to prevent a second fermentation which would spoil the product. The precipitate is strained off on large canvas filters supported by bamboo canes, and the nearly black mass is pressed, dried, and cut up into cubic cakes (see Figs. 97 and 98). The indigo of commerce is a dark blue solid which on being rubbed or pressed by any hard body presents a bright, copper coloured shining surface. It is insoluble in water or alcohol, but dissolves in hot strong sulphuric acid, forming a permanent blue liquid containing indigo-sulphonic acids, which remain in solution when mixed with water and are used in dyeing.

The cultivation of the indigo plant in India has, down to recent years, occupied a very large acreage of ground. It appears from the Agricultural Statistics of India, published by the Department of Revenue and Agriculture (Vol. I. 1904, pp. 2, 3, and 350; Vol. I, 1913, pp. 8-9), that in 1884-5 the land devoted to this crop amounted to 897,917 acres. This gradually increased down to 1896-7 when the area under cultivation was 1,583,808 acres, and the weight of indigo produced was 168,673 cwts or 8433 tons. The value of "fine Bengal" indigo between the years 1812 and 1833 varied from 5s. 6d. to 15s. per pound. The value in 1888 averaged 3s. 9d. per pound, and in 1908 it had come down to 2s. 6d. to 2s. 9d. per pound. But synthetic indigo costing at the same time even less the price of the natural product had to be further reduced; the price of synthetic indigo is now (1935) given as 3s. 5d. per pound, but it must be remembered that dyestuff prices are on the average twice the pre-war rates.

The rapidity with which the cultivation of indigo in India has fallen off is shown by the following table of figures.

PRODUCTION OF INDIGO IN BRITISH INDIA

Year.	Acreage.	Amount (cwts.).
1896-7 . . .	1,584,000 ..	168,700
1909-10 . . .	295,706 ..	40,000
1921-2 . . .	329,000 ..	67,000
1925-6 . . .	134,000 ..	28,000
1926-7 . . .	104,000 ..	19,000
1927-8 . . .	67,000 ..	11,000
1928-9 . . .	80,000 ..	15,000
1929-30 . . .	71,000 ..	14,000

There is little doubt, from these figures, that the cultivation of indigo can now only be regarded as a very minor industry, and there seems little hope of its revival.

There is naturally some conflict of statement as to the relative merits of the natural and synthetic dye-stuffs from the point of view of the dyer. On the one hand, such statements as the following extracted from a paper in the *Kew Bulletin* (No. 8, 1910, p. 285) have been made :

“ There appears to be no doubt as to the superiority of the natural over the artificial product for dyeing purposes, and this is not where the fault lies ; but it does seem very problematical as to whether good quality indigo can ever be produced under cultivation at so cheap a rate as that at which the synthetic substance is now manufactured. It has been stated that the two products are more effective when mixed in equal proportions, and if this be always true it is possible that it may contribute more than anything else to the support, and perhaps to the expansion of the cultural industry.”

On the other hand it is asserted that synthetic indigo is capable of producing all the varieties of shade previously obtained by the use of the natural dye and equally permanent, with the advantage of uniformity of composition and freedom from impurities which saves much trouble to the competent dyer. In view of the almost complete elimination of natural indigo from the modern dye works, it seems reasonably certain that this point of view is the correct one.

Some sympathy may perhaps be felt for the Indian planter, but there are many aspects of the cultivation of indigo which must be considered. In the first place, it has been urged that indigo as a crop has always been uncertain and that its sub-



FIG. 95.—INDIGO BEATING THE VAT

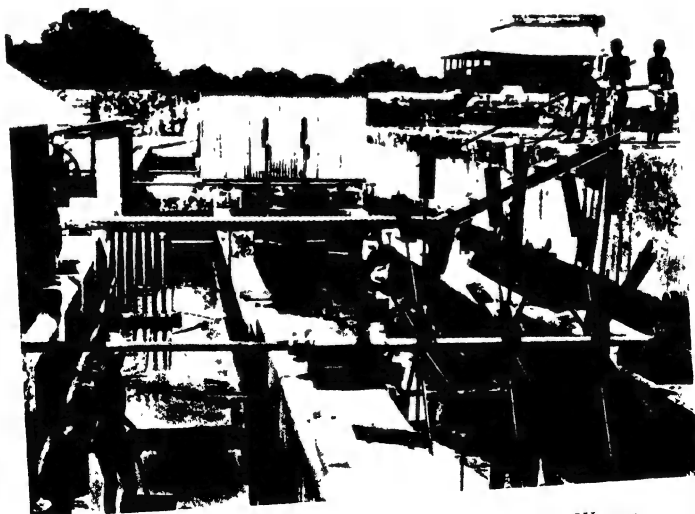


FIG. 96.—INDIGO BEATING VAT WITH WOODEN WHEEL



FIG. 97 -INDIGO BOILERS AND FILTERING TABLE



FIG. 98 INDIGO DRYING HOUSE

stitution by crops which supply foodstuffs would be on the whole an advantage to the country. Secondly, it must be realised that for many years, as long as the industry was reasonably successful, nothing was done in the way of a botanical study of the crop for the selection of the best type of plant and for determining the best conditions of cultivation. It is true that a half-hearted effort in this connection was made after the war, and although it was partly successful it came much too late; if experimental work had been started twenty years earlier the situation to-day might have been very different.

The artificial production of indigo from constituents of coal-tar has a long scientific history, but in this case, as in so many other cases, success in the laboratory does not necessarily imply success in the factory. For while in the former case the purposes of science and additions to knowledge are the chief objects in view, in the latter the process ultimately to be adopted is determined not alone by practicability but ultimately by the *cost*. The various synthetic methods which have been proposed since 1875 are to be found in the chief textbooks of organic chemistry. Here we can only review those which have had a practical success and form the present source of the synthetic dye.

One other point for consideration has also had a large influence in the choice of the process adopted. The question is which of the hydrocarbons present in coal-tar is to be chosen as the starting point, supposing the operations leading to the dye being about equally suitable? This can only be answered by calculating the probable demand for the synthetic product, and ascertaining the probable amount of the requisite coal-tar hydrocarbon available. These considerations it was, which, according to Dr. H. Brunck, director of the great colour works at Ludwigs-hafen, led to the abandonment of the otherwise successful process which depended on toluene, in favour of a process which starts from the far more abundant naphthalene obtained from coal-tar.

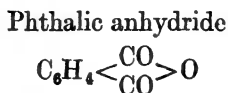
The raw material of one of the modern processes is then naphthalene, and the successive steps can be most concisely indicated by the following formulæ.

Naphthalene heated with fuming sulphuric acid and a small quantity of mercury is oxidised into phthalic acid. The sulphuric acid is reduced to sulphur dioxide which, by the modern contact process, is converted back again into sulphuric acid. It is

therefore the oxygen of the air which thus indirectly acts on the naphthalene.

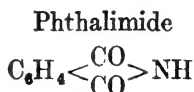


Phthalic acid when heated (sublimed) loses water and is converted into

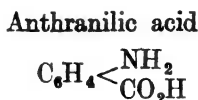


In a more recent process naphthalene is oxidised directly to phthalic anhydride by passing its vapour, mixed with air, over a catalyst consisting of vanadium pentoxide.

By heating the anhydride in presence of ammonia it is converted into



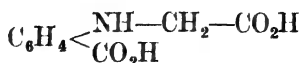
This compound under the simultaneous action of alkalis and chlorine in the form of alkaline hypochlorite yields



The next step is the conversion of anthranilic acid into phenyl-glycine-ortho-carboxylic acid by interaction with monochloro-acetic acid. This reagent has to be manufactured separately, but the electrolytic soda industry yields the necessary chlorine, together with caustic soda which is also required in various stages of the process.

Lastly, the phenyl-glycine acid is melted with alkali or a substitute for it, and the solution of the mass in water is oxidised by exposure to a stream of air whereby indigo blue is precipitated.

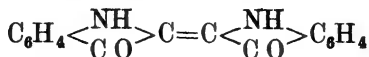
Phenyl-glycine-ortho-carboxylic acid



produces first indoxyl



and by oxidation indigo blue



The introduction of sodamide, NH_2Na , an alkaline substance which also acts powerfully as a dehydrating agent, has led to the development of another process which runs on simpler lines, starting from benzene as the primary material.

When aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is treated with chloroacetic acid phenyl-glycine, $\text{C}_6\text{H}_5\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, results. And this compound, heated with sodamide or with sodium in the presence of ammonia, gives a good yield of indigo. The intermediate compound is indoxyl or its sodium derivative as already explained.

Indigo being insoluble in ordinary aqueous solvents special methods have to be used in applying it as a dye. One which makes use of the solution in sulphuric acid has already been referred to, but the other, of very ancient origin, is dependent on the reduction of the blue to *indigo white*, a colourless substance, which forms soluble salts with alkaline solutions.

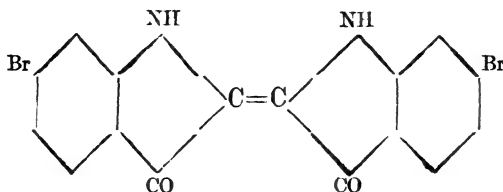
At one time the vat was prepared by mixing the blue indigo with a solution of lime or caustic potash or soda and green vitriol (sulphate of iron), or with vegetable matter such as bran. The modern method is to use sodium hyposulphite, known technically as hydrosulphite or "hydros," which is manufactured almost exclusively for this purpose. The result in any case is a yellow liquid, containing indigo white, which on exposure to the air absorbs oxygen and reproduces the blue. Hence for dyeing cotton the cloth is immersed in the alkaline liquid, and when saturated it is exposed to the air and the blue is deposited in the insoluble form within the fibre. Insoluble dyes which have to be applied in this manner are called by the general name of "vat dyes."

A very important advance in connection with these dyes has been made recently. Indigo white, and similar reduced forms of the vat dyes, could not be marketed in this form because they were so readily oxidised by air; it was necessary, therefore, for the dyer to carry out the reduction. It has been found, however, that certain derivatives of indigo white and related substances, the chemical description for which is the "sodium salts of the sulphuric acid ester," known technically as *indigosol* or *soledon* dyes, are quite stable and soluble. They can be sold

in the reduced form, applied directly to the fibre and then decomposed to the indigo white form and oxidised to the coloured state in one operation.

Some of the derivatives of indigo produced by the introduction of bromine into the molecule are important dye-stuffs which are known in the trade as Ciba dyes.

In this connection an interesting discovery has resulted from the modern investigation of the purple dye extracted as in ancient times, from a species of *murex*, a mollusc found in the Mediterranean, and generally referred to as Tyrian purple. It is now known to be dibromindigo with the following formula :



The next dyestuff which may be described is very different in constitution from indigo, but is interesting not only on account of its great practical importance, but because it has a very similar history. The substance referred to is the red colouring matter of the madder root.

The madder plant is a herbaceous perennial, *Rubia tinctorum* (Nat. Ord. *Stellatae*), very nearly allied to the common goose grass or cleavers of our hedges. The *R. peregrina*, which is regarded by Hooker (Bentham's *British Flora*) as probably a mere variety of *R. tinctorum*, is found in the southern and western parts of Britain and of Europe. The use of the root as a dye can be traced to very ancient times, as it is not only mentioned by Pliny, but the red dye-stuff has been recognised in the mummy cloths of Egypt. It has been cultivated for centuries in the Levant, and in 1766 was introduced into the south of France by Jean Althen, to whom a statue was erected at Avignon. The chief colouring matter in madder is called *alizarin*, it is accompanied by several others of which the most important is named purpurine. Alizarin was isolated for the first time by Robiquet and Colin in 1828. The composition of this substance remained for many years a mystery. It was at one time supposed to be a derivative of naphthalene, and many attempts were made

to produce it synthetically from that substance, but it was not till about 1868 that its true nature was discovered and its connection with anthracene was established. Anthracene is a hydrocarbon, $C_{14}H_{10}$, which occurs among the least volatile portions of coal-tar, and up to this time it had been totally neglected and left in the pitch. Its relation to anthracene being once known a key was obtained to its constitution, and in 1869 patents were taken out for its production by Caro, Graebe, and Liebermann, followed only one day later by W. H. Perkin.

This was the first natural colouring matter to be produced synthetically and one of the most important, inasmuch as alizarin and its derivatives and associates are employed in the production of cotton prints all over the world, and are capable of giving a great variety of colours. Here it must be explained that alizarin and the allied colouring matter purpurine are often referred to as *adjective* dyes, because they do not dye either animal or vegetable fibre without previously impregnating the fibre with some basic substance, such as alumina or oxide of iron, chromium, or some other metal. The colouring matter unites with such substances forming chemical compounds called *lakes* which are insoluble in water. The metallic base introduced is called a *mordant*, and each colouring matter produces a different colour on the cloth by varying the mordant. Thus alizarin with

Iron oxide gives a violet colour

Chromic oxide gives a brown colour

Aluminium oxide gives a bright red colour

A recent improvement in these mordant (or adjective) dyes is the combination of the metallic base together with the colouring matter in one compound, thus saving an operation in the dyeing process. These new dyes are known by the name of *neolan* colours.

Dyes which attach themselves directly to the fibre are spoken of as *substantive*, or *direct* dyes.

A large amount of knowledge has been gained in recent times as to the chemical constitution of the substances of which wool and silk fibres are composed, and the facts have given much assistance toward the conception of a comprehensive theory of dyeing. For reasons to be explained later no one theory has yet been completely established, and much remains in obscurity.

It would perhaps be advisable at this point to remind the

non-chemical reader of the meaning attached to the words acid and base.

Acids are substances such as acetic acid in vinegar, tartaric, citric, and malic acids found in fruit, and the mineral acids, sulphuric, nitric, and hydrochloric acids. These are all soluble in water, and when sufficiently diluted have a sour taste and cause chalk and other carbonates to effervesce when mixed with them.

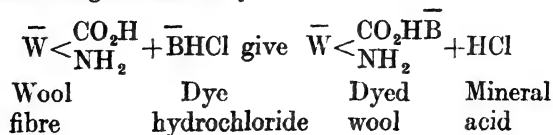
Basic substances are those which when mixed with an acid in due proportion destroy the acid taste and give rise to a new compound called a salt. Basic substances are divisible into two classes, of which one is represented by ammonia, aniline, and other organic bases. These combine directly with acids. The other class of basic compounds includes hydrated oxides of metals, such as caustic soda, lime, alumina, etc. When these are mixed with an acid they produce a salt, and the oxygen of the base unites with the hydrogen of the acid forming water.

The word salt is used in a very wide sense by the chemist, and though common salt is the most familiar of all salts, they are not all, like it, soluble in water and neutral, that is neither sour nor soapy to the taste.

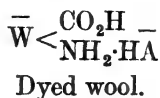
Wool and silk are known to be composed chiefly of substances which are very complex in constitution, but when decomposed they yield peculiar compounds which behave under one set of conditions as acids, and under another as bases. The simplest example of such compounds is *glycocoll* (now commonly called glycine) or amino-acetic acid, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which will produce a salt either by combining with a base because of the acidic CO_2H group or, in virtue of the ammonia residue, NH_2 , which it contains, by combining with an acid such as hydrochloric acid.

This peculiar property is shared by the substances of which silk and wool consist, and they are therefore able to enter into chemical combination with dyeing matters of both an acid and basic character.

When, for example, silk or wool is dyed with magenta, which is a salt of a basic dye, the colour base leaves the mineral acid with which it is combined and unites with the acidic constituent of the fibre, while the mineral acid is left in the bath. This may be expressed diagrammatically as follows :



In a similar manner the process of dyeing by acidic colours, such as picric acid, may be represented. In this case a combination occurs in which the colour acid, $\text{H}\bar{\text{A}}$, unites with the ammonia residue of the fibre, thus :



Although this may not represent exactly and completely the actual process occurring in the dye-bath, it probably gives a picture which is a general approximation to the truth. The study of the phenomena of surface attractions during recent years may perhaps require the theory to be modified or probably additions may have to be made.

It has long been known that many substances such as charcoal have the property of withdrawing colouring matters from solution and the fact has long been turned to practical account in the refining of sugar. The syrups from which white sugar is to be obtained are filtered through thick beds of bone charcoal, where the brown uncrystallisable substances present are *adsorbed* into the substance of the charcoal, while the sugar is retained in solution. This power possessed by charcoal seems to be connected with the extent of surface of the particles of which it is composed, and it is shared to a greater or less extent by other substances which can be got into a fine state of division, notably by metals such as platinum and palladium, metallic oxides and hydroxides such as alumina, and even by fine sand and powdered glass, though in an inferior degree.

The fibres of silk, wool, and cotton consist of substances possessing more or less the character of colloids (chap. XIII). When immersed in the dye-bath the deposition of the colouring matter takes place in a somewhat irregular manner, some of it forming a layer external to the fibre and some penetrating into the interior. This can be seen under the microscope. The probability therefore is that the attachment of the dye-stuff to the fibre is due in the first instance to mere surface attraction or adsorption, and that the colouring matter is then retained, partly, at least, by chemical combination. Some dyes can be removed from dyed fabrics by ordinary neutral solvents such as alcohol. This does not prove that chemical combination has not taken place between the dye-stuff and the fibre, and that

the union is comparable with mere surface adhesion: it only seems to indicate that the saline combination formed is weak in character. The picric acid combination with the basic elements in wool fibre, for example, may in fact be similar to the combinations formed by weak bases or acids which are more or less completely decomposed by water. Thus urea combines with nearly all acids forming crystalline compounds which, however, possess a definite composition only when deposited in the presence of excess of acid. Any attempt to recrystallise from pure water leads to the reproduction of the base, while the acid passes into the liquid.

Linen and cotton consist of *cellulose*, a compound or mixture of compounds which possesses neither acid nor basic character, and accordingly it appears at first sight that dyes do not attach themselves to the fibre in consequence of chemical combination of the kind just referred to. In spite of this, the view has been recently expressed that it is by no means certain that cellulose molecules are not able to unite chemically with molecules of dyestuff. It is quite probable that both chemical combination and adsorption are operative; when dyeing with a mordant it is believed that the latter factor is the more important.

From these facts it appears that the process by which colouring matters become attached to vegetable or animal fibres and to mordants is more complicated than was supposed, and the phenomena of the dye-bath are for the present not fully understood.

Cotton is frequently dyed by means of substantive dyes which do not require the application of a mordant. Safflower (*Carthamus tinctorius*) yields a natural red colour which is one of these, and many artificial dyes made from coal-tar are now used as direct cotton dyes. The first to be discovered was Congo Red.

In many cases of this kind the retention of the colour by the vegetable fibre may be due to the fact that the fibres of cotton and flax are hollow, and a portion of the dye becomes imprisoned within these microscopic tubes, and by a peculiar surface action of the cellulose it is retained there. There is no formation of a lake, and the cotton dyes are less resistant to soap and other agents than those which have been fixed by a mordant.

It is of interest to note in this connection that many dyes which are quite satisfactory for cotton were found to give



FIG. 99.—VACUUM OVENS FOR DRYING DYESTUFFS
(By courtesy of *British Dyestuffs Corporation, Ltd.*)



FIG. 100 MANUFACTURE OF AZO DYES

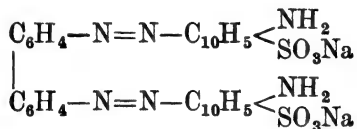
(By courtesy of British Dyestuffs Corporation, Ltd.)

uneven results with artificial silk made from cellulose. The main difference between this material and cotton, with which it is identical chemically, is that the artificial silk consists of rod-like, that is solid, threads, in place of the hollow threads of cotton. Special direct dyes, known as *icyl* dyes, are generally used for viscose artificial silk (see chapter XXIV); these seem to have a strong attachment for cellulose.

A large and important class of dye-stuffs, known as the azo-dyes, must not be overlooked, though it is impossible to explain fully to the non-chemical reader the nature of their constitution. They may be regarded as made up of two proximate constituents, one of which is a compound formed by the action of nitrous acid on a base such as aniline, naphthylamine, benzidine, while the other is a phenol or its sulphonic acid, or a base (amine). These two being brought together in solution "coupling" occurs, and the new colouring matter is produced. This always contains an association of nitrogen atoms



which may exist in the molecule several times over, and serves as the link to which are attached the two proximate constituents of the colour molecule. These colouring matters have consequently a rather complex constitution, which may be illustrated by the formula of Congo Red mentioned above.



In some cases the coupling process may be effected in the fibre itself, the diazo-compound being formed by immersing the fabric to be dyed, first in a solution of the base, then in a solution of nitrous acid, and lastly in the bath in which coupling takes place with a phenolic or basic substance.

Colours of this class are generally called *ingrain* dyes.

The invention of cellulose acetate silk, sold commercially as Celanese, raised a new problem in dyeing; at first ingrain dyes, known as *ionamines*, were used, but these have given place to the *dispersol* or *duranol* colours. These substances come on the market in the form of pastes, the finely divided dye material being mixed with an oil and soap; on addition to water it forms

a colloidal suspension, the particles in which are adsorbed uniformly by the acetate silk.

The following table contains a synopsis of the main types of synthetic dyestuffs classified according to their method of application to the fibre; one or two of the earliest discovered examples are given in each case.

MODERN OR SYNTHETIC DYES

Class I. Dyes with a basic character. These colours are applied directly to wool and silk. They are mainly used for cotton, with the aid of an acidic mordant, generally tannic acid.

Mauve	discovered 1856
Magenta	„ 1860
Bismarck Brown	„ 1865

Class II. Dyes with an acidic character. These colours are applied directly to wool and silk from an acid bath.

Picric acid	discovered 1771
	applied 1855
Aniline Blue	discovered 1862
Azo-scarlets	„ 1876

Class III. Acidic dyes requiring a metallic mordant. These dyes are fixed to mordanted fabrics, the colour produced being due to an insoluble salt. (Dye+mordant=lake.)

Alizarin Red	discovered 1868
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and other dyes of the alizarin group, including Alizarin Blue and Alizarin Green, Gambine Yellow, and certain other Azo-dyes.

Quinone-oxime Dyes	discovered 1875
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Class IV. Direct or substantive dyes. Colours dyeing unmordanted cotton or linen directly in neutral or alkaline baths.

Congo Red Series	discovered 1884
Cotton Black (Diamine Black)	„ 1889
Chlorazol Blue	„ 1898

Class V. Vat dyes. These are applied to the fibre in the reduced state and then oxidised by air or by other means.

Synthetic Indigo	discovered 1897
Indanthrene dyes	„ 1901

Class VI. Ingrain dyes, in which the actual dye is produced by a chemical coupling on the fibre, are mainly used for cotton.

Ingrain Azo-dyes (Ice colours)	discovered 1880
Ionamines	„ 1922

Class VII. Sulphur dyes. These dyes are complex substances containing sulphur; they are insoluble in water, but soluble in sodium sulphide solution, from which the fabric is dyed. The material (cotton) is subsequently oxidised in air or by treatment with a metallic salt.

Cachou de Laval	discovered 1873
Immedial Black	„ 1897

For further information on the subject of dyes and dyeing, the reader should consult *The Synthetic Dyestuffs and their Intermediates*, by Cain and Thorpe, recently completely revised by Thorpe and Linstead.

CHAPTER XXII

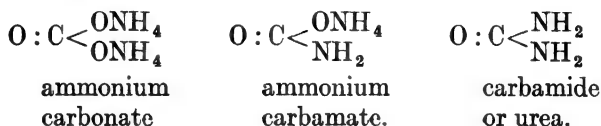
DRUGS, HORMONES, AND VITAMINS

It is perhaps worth while, before proceeding further, to review very briefly the history of the processes by which the chemist has gradually learnt how to build up very complicated substances by bringing together the elements of which they are composed, in other words to produce such substances by what is called synthesis. The first case of the production of a compound previously known only as a result of processes going on in organic living matter is that of urea.

This is the chief nitrogenous excretory product in mammalia, a smaller amount being thrown off by other animals such as birds. The source of the nitrogen is the protein constituents of the food, and a man on ordinary diet excretes on the average 30 to 35 grams (1 oz. to 1¼ oz.) per diem, almost entirely in the urine.

By the transformation of ammonium cyanate, NH_4CNO , a salt which can be made from wholly *inorganic* materials, urea

$\text{CO}(\text{NH}_2)_2$, was obtained by Wöhler in 1828. As the formula indicates, this change is due to a mere rearrangement of the elements present in the molecule, without addition or subtraction of anything. Such a transformation is called in chemical language an isomeric change. Comparatively little notice was taken of this remarkable discovery for many years, and it was reserved for later times to recognise its significance. Forty years later a Russian chemist, Basaroff, discovered that urea might be formed by the simple action of heat on ammonium carbonate, whereby it loses the elements of water in two stages and leaves a residue which is urea. Here again a rearrangement takes place, but it is accompanied by elimination of hydrogen and oxygen in the form of water.



The production of urea in the animal body is, apparently, closely related to this change, the primary materials being the ammonia and carbonic acid of the blood which unite to form ammonium carbonate or carbamate.

Another organic compound produced from inorganic substances in the chemical laboratory was acetic acid, which was synthesised by Kolbe in 1845. Again very little attention was given to the discovery owing to the state of ignorance then prevalent in the domain of organic chemistry.

It was only some years later that a systematic study of synthetic processes was undertaken by Berthelot¹ the famous French chemist. He showed how, by starting from the elements and from mineral substances, carbon can be combined step by step with hydrogen, then with oxygen, and again with nitrogen, producing thereby organic compounds, some identical with

¹ Pierre Eugène Marcellin Berthelot was born in Paris in October 25th, 1827; he completed a full medical course, but was ultimately led to adopt a purely scientific career. Beginning with the humble appointment of lecture assistant to the Professor of Chemistry in the Collège de France, he later became Professor in the École Supérieure de Pharmacie, and finally Professor of Organic Chemistry in the Collège de France, a post he held till his death on March 18th 1907. In 1889 Berthelot succeeded Pasteur as Perpetual Secretary of the Academy of Sciences, and in 1900 he became one of the forty French Academicians. He was a prolific investigator and writer, and his work covered a very wide range of interests, which included the synthesis of fats and other organic



W. Lenthérol

certain products of nature, others only analogous thereto, but at the same time serving as starting-points for the formation of natural organic compounds. A single example taken from Berthelot's work will suffice by way of illustration. By heating carbon (coke or charcoal) in the electric arc surrounded by an atmosphere of hydrogen acetylene C_2H_2 is formed. By an easy process acetylene can be made to combine with more hydrogen so as to produce ethylene, C_2H_4 . Ethylene dissolves in concentrated sulphuric acid, and the compound thus formed when mixed with water unites with the elements of water and, distilled, yields *alcohol*, C_2H_6O . The alcohol thus formed is identical in every respect with alcohol produced by fermentation of sugar. The synthetic process is so practicable that a company was at one time actually formed with the object of manufacturing alcohol from common coal-gas, of which ethylene is a constituent; although this was not successful it is remarkable that the same method is now being used in the United States to obtain alcohols from ethylene, and related compounds, present in the gases obtained during the refining of petroleum.

The development of the same idea as that which was the basis of Berthelot's experiments has led in later times to the building up of numberless chemical compounds previously known only as limited products of animal or vegetable life. The first example of the application of this principle on the large scale was the manufacture of salicylic acid, by a method discovered by Kolbe in 1874 in which phenol (carbolic acid) present in coal-tar is the starting-point.

The phenol is dissolved in caustic soda producing sodium phenate, C_6H_5ONa , and this compound, saturated with carbon dioxide gas under pressure at a slightly elevated temperature, is converted into sodium salicylate, $C_6H_4(OH).COONa$, from which, of course, the acid is easily made.

Since that time the number of syntheses turned to practical account is very large. Two examples have already been

compounds, thermochemistry, chemical equilibrium, explosives and explosion waves in gases, and Greek and Arabian alchemistic writings. During his life Berthelot received many honours both in France and elsewhere; he was elected a Foreign Member of the Royal Society in 1877, and awarded its Davy Medal in 1883, and the Copley Medal, the highest distinction bestowed by the Royal Society, in 1900. For further details the Memorial Lecture, given by Professor H. B. Dixon (*Journal of the Chemical Society*, 1911, p. 2353), should be consulted.

mentioned in the two dye-stuffs, alizarin and indigo, of which the history has already been given. Many other cases will be referred to in the following chapters, where it will be noticed that though the hydrocarbons extracted from coal-tar are the fertile parents of a whole host of new substances, others are actually derived from the more simple combinations of the elements themselves, starting from carbon itself and bringing it into a state of union with hydrogen or with the gases of the atmosphere, oxygen and nitrogen.

With this by way of preliminary we may now proceed to enumerate, rather than describe, a few of the more prominent among medicinal agents which are the products of the chemical laboratory derived from materials of inorganic origin. These are commonly referred to as synthetic drugs, to distinguish them from those which, like quinine, morphine, strychnine, aloin and others, are provided by nature, and which constitute the active principles of plants which have long supplied active remedies in the treatment of disease. These principles exist ready formed in the plant, and are not in any way transformed in the chemical laboratory, but are merely separated in a pure state by suitable solvents or otherwise from the vegetable tissues which contain them.

Before proceeding to describe the origin of some of the most modern of chemical drugs the reader may be reminded that previous generations have already enjoyed the use of some of the agents originating in the chemical laboratory. The most familiar of anæsthetics, "the gas" used by every modern dentist, was breathed for the first time by Sir Humphry Davy so long ago as 1798, and in the earliest of his works he describes his "Researches Chemical and Philosophical chiefly concerning Nitrous Oxide and its Respiration" (1800).

Ether has been known from the times of the alchemists and from its being produced by the action of strong sulphuric acid on alcohol, it was called in those days *oleum vitrioli dulce*. Its use as an anæsthetic belongs exclusively to quite modern practice; it is generally associated with chloroform.

The other famous anæsthetic, chloroform, was discovered by Liebig in 1832, but its remarkable physiological action was recognised in 1847 by Sir James Young Simpson, who thus conferred on suffering mankind for all future time a benefit of incalculable value.

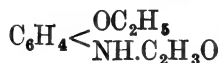
The alkaloids of opium and those of cinchona bark and many other vegetable principles had also been introduced into regular medical practice long ago. The characteristic of our own time in respect to medicine arises from the great advances which have been made in the knowledge of physiology and theoretical chemistry, and recognition of the interdependence of the one on the other.

A brief account of some of the more prominent among chemical medicines now follows.

Acetanilide, known as *antifebrine*, is produced by the action of acetic acid on aniline, and is represented by the formula $C_6H_5NH.C_2H_3O$.

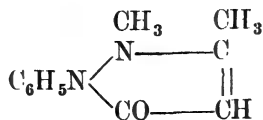
Acetyl Salicylic Acid, still known as *aspirin*, is the acetic derivative of *Salicylic Acid*, which is itself orthohydroxy-benzoic acid, $C_6H_4<\begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$. This important compound exists in the meadowsweet and other plants, but is manufactured by heating sodium phenate, C_6H_5ONa , in the presence of carbon dioxide, as already explained. From the product dissolved in water salicylic acid is precipitated by the addition of hydrochloric acid.

Another acetyl compound is *phenacetin*, which is the para acetamino-derivative of phenetole $C_6H_5.OC_2H_5$. The formula is therefore :

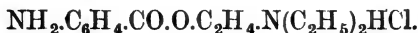


Picric Acid is a pale yellow crystalline substance produced by the action of nitric acid on phenol. It is trinitrophenol, $C_6H_2(NO_2)_3.OH$, and is extensively used as a yellow dye for silk and wool (p. 332) and as an explosive (p. 399). In medicine it is chiefly employed as a lotion for burns.

A somewhat more complicated compound is *antipyrine*, called *phenazone* in the *British Pharmacopæia*. This is obtained by a succession of steps which begin with aniline and ultimately give the compound which, in chemical language, is dimethylphenyl pyrazolone, and the formula is

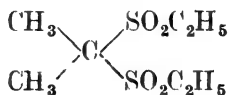


Novocaine is one of the modern local anæsthetics. This substance is the hydrochloride of diethylamino-ethyl-*p*-aminobenzoate

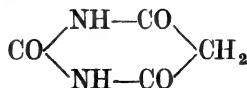


One of the most remarkable compounds which has come into use during recent years is *formaldehyde*. This is obtained on a large scale by bringing the vapour of methyl alcohol (wood spirit) mixed with air into contact with heated platinum or copper. The formaldehyde produced is a gas, but dissolves readily in water, and a solution containing nearly 40 per cent is sold under the name of "formalin." This is used as a disinfectant and antiseptic. A very minute quantity of it added to milk, for example, will prevent change for many days. It has also the remarkable property of rendering gelatine in any form, such as glue, insoluble in water, whence many applications of this property to technical purposes. When brought into contact with ammonia it is converted into a solid crystalline substance, hexamethylene tetramine $(\text{CH}_2)_6\text{N}_4$, used in medicine under the name *hexamine*, *urotropin* or *formin*. Both formaldehyde and hexamine are now employed on a large scale in the manufacture of synthetic plastics (chapter XXV).

A well-known soporific goes under the name *sulphonal*. It is dimethylmethane diethylsulphone



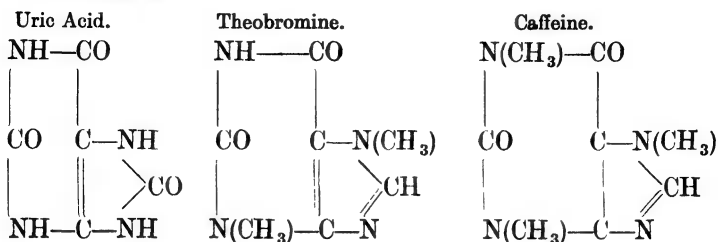
Veronal is the name of a compound which, under the new designation *barbitone*, has found its way into the *British Pharmacopœia*. Its chemical nature is indicated by the name diethylbarbituric acid. Barbituric acid, otherwise known to the chemist as malonyl-urea, has the formula



Its sodium salt is used medicinally under the name *medinal*.

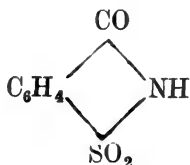
Malonyl-urea has an interest apart from its use in medicine, arising from its relationship on the one hand to uric acid, an important excretory product of the animal organism, and on the other to theobromine and caffeine, the bases found respectively in cocoa and tea or coffee.

Formula of



All these compounds have been produced synthetically from purely chemical materials and independently of animal or vegetable agency.

Among the many synthetical products which have become familiar in our own time is *saccharin*, a compound which is reputed to have a sweetening power four to five hundred times the sweetness of cane sugar. Saccharin, or *gluside* as it is called in the *British Pharmacopæia*, is orthosulphamido benzoic anhydride



It is produced by a series of operations which have for starting-point the hydrocarbon toluene obtained from coal-tar. It is used as a substitute for sugar in the diet of patients suffering from diabetes and other disorders.

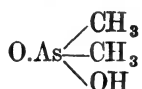
All the preceding compounds and many others are officially recognised as medicinal agents by the General Medical Council by whom the *British Pharmacopæia* is issued. But many other chemical compounds used for medicinal or dietary purposes have been the subject of experiment. Some have had their utility established and have been adopted with practice, while many others, after a brief notoriety, have returned to oblivion.

The discovery of new remedies depends more and more on a combination of chemical and physiological knowledge. No better illustration of this principle could be adduced than the case of the remarkable compound "salvarsan," or 606, the use of which was introduced into medicine by the late Professor Ehrlich.

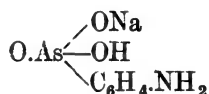
Salvarsan is an artificial chemical compound containing the

element arsenic in such a condition that it does not produce the ordinary effects of arsenical poisoning. It possesses the property of seeking out and destroying the specific organism of syphilis, the *spirochaeta pallida*.

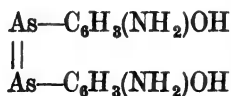
Salvarsan does not represent the first attempt to use arsenical compounds for medical purposes. Common white arsenic, the arsenious oxide As_2O_3 , has long been recognised as a valuable alterative and tonic medicine when given in minute doses. It is also known to act as a dangerous poison in quantities exceeding a small fraction of a grain. Some fifty years ago cacodylic acid (dimethylarsinic acid)



was tried in cases of tuberculosis, and arsenic acid itself was reported to have some value. Later a number of arsenical organic compounds were prepared by the French chemist Béchamp and others. Among the rest a substance named "atoxyl" was introduced into medicine. Its constitution was, however, unknown and misrepresented till, in 1907, Ehrlich, in conjunction with A. Berthelm, proved that atoxyl is the sodium salt of para amino phenyl-arsinic acid, the formula of which is



The use of atoxyl has been practically abandoned in favour of *salvarsan* which is the hydrochloride of dioxydiaminoarsenobenzene,



or of a soluble derivative of salvarsan known as *neosalvarsan*. The rapid rise into notoriety of these remarkable substances is known to all the world, but it appears to be still doubtful whether they are effectual in all cases, and their action occasionally becomes poisonous. This is probably partly due to the fact that on exposure to the air they readily undergo oxidation yielding more poisonous compounds.

A large number of researches have been carried out on aromatic compounds containing the elements phosphorus, arsenic, and antimony, which in the periodic scheme are members of the same family as nitrogen. Some of these may hereafter be found to possess medicinal properties similar to those of salvarsan and, it is to be hoped, less dangerous. Announcements from time to time appear in the newspapers and in the medical press; one of these is to the effect that the German firm of Bayer has produced a new drug, called "Bayer 205," which is said to prevent the development of the micro-organisms associated with sleeping sickness, the great scourge of Central Africa.

Time alone can show whether these expectations are justified.

On a previous page several of the natural drugs provided by the vegetable kingdom were mentioned. Of these the most important by far are those which are familiarly known as "alkaloids" inasmuch as the majority of them possess very powerful physiological action, and in many cases act as violent poisons when introduced into the animal economy either by the mouth or by hypodermic injection into the circulatory system.

It is only necessary to mention strychnine, morphine, and atrophine, all of which are used in medicine. These and many other substances of the same class have been known for a long time, approaching a century. But beyond the fact that they contain beside carbon, hydrogen, and commonly also oxygen, together with nitrogen, little was known until recent times as to their chemical constitution. They agree in possessing the power of uniting with acids forming definite and usually crystalline salts. This property is connected with the nitrogen they contain, and down to about sixty years ago they were assumed to be derivatives of ammonia, and the name *alkaloid* applied to them all had reference to the basic or alkaline character exhibited more or less strongly by every one. A considerable number of basic substances have been discovered in animal tissues or in products of decomposition and in a few cases these are identical with alkaloids derived from vegetable substances. Adenine, for example, is a base of comparatively simple composition with the formula $C_5H_5N_5$, which occurs not only in the pancreas but in small quantity in tea, beetroot, and shoots of bamboo. Its constitution is perfectly well known, not only from a study of its products of decomposition, but from the fact that it has been produced synthetically in the laboratory.

Another case of a natural alkaloid which has been produced by artificial processes is coniine, the poisonous principle of hemlock (*Conium maculatum*). This is a colourless, oily substance, having the formula $C_8H_{17}N$, which is obtainable from the hemlock plant or fruits by distillation with a solution of sodium carbonate. It rotates the plane of polarisation to the right. The artificial product is optically inactive as it consists of equal quantities of two stereo-isomeric bases, the one rotating to the right, the other to an equal extent to the left. These were separated from each other by Ladenburg by fractionally crystallising the tartrates, and the artificial right-handed base was found to be identical with the natural.

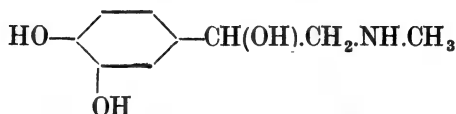
Several other well-known alkaloids, such as nicotine, cocaine, papaverine and narcotine, have been synthesised in the chemical laboratory, but quinine, morphine, and strychnine have so far defied the chemist.

HORMONES

In connection with substances used in medicine mention must be made of the *hormones*, which have often been called "chemical messengers"; they differ from the substances dealt with in the earlier portion of this chapter because in a normal human being they are produced by the ductless or "endocrine" glands and pass straight into the blood stream, and it is only when these glands fail in their functions that the hormones are supplied from without. These substances, although required only in very minute amounts, are apparently responsible for regulating a number of vital processes, and in their absence some serious abnormalities result. During the present century chemists in co-operation with physiologists have succeeded in isolating a number of these hormones in a pure form as crystalline substances: in some cases their chemical structural formulæ have been determined and a few have even been synthesised in the laboratory and found to be identical with those occurring in the living organism.

The first hormone to be obtained synthetically was *adrenaline*, or *epinephrine*, as it is called in the United States; it is normally produced by the supra-renal glands, situated above the kidneys. The defective functioning of these glands leads to Addison's disease, and according to Dr. (now Sir Henry) Dale "there is evidence that the constant presence of traces of this hormone (adrenaline) in the blood is a necessary condition for the main-

tenance of a healthy tone." Adrenaline was first isolated, in a pure chemical form as white crystals, in 1901 by Professor Takamine in Japan, whose work was based on the earlier discoveries of Professor J. J. Abel of the Johns Hopkins Medical School in the United States; the source of the adrenaline was the supra-renal glands of animals. Shortly afterwards its chemical structure was established by various workers in England and Germany as

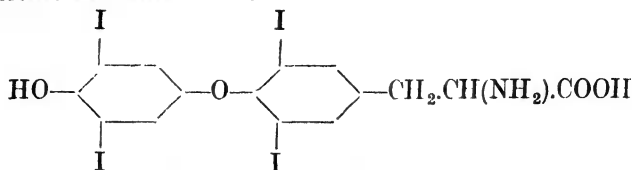


where the hexagon as usual represents a benzene nucleus of six carbon atoms (p. 311). In 1904 it was synthesised in the laboratory, but the product, like most synthetical substances, does not rotate the plane of polarisation of light, whereas the natural adrenaline is optically active and rotates the plane to the left, that is to say it is *lævo*-rotary. The synthetic product was resolved into its two isomeric forms, and the *lævo*-rotatory form was found to be identical in its physiological effects with the hormone from natural sources. It is a striking fact that the *dextro*-rotatory substance, which is otherwise chemically identical with adrenaline, has only one-fifteenth the physiological activity of the *lævo*-rotary compound. The chief use of adrenaline in medicine at the present time is for addition to novocaine, the local anæsthetic for minor surgical operations; the adrenaline tends to constrict the small blood vessels and so prevents bleeding.

The active principle of the thyroid gland, known as *thyroxine*, which is actually produced by the gland in the form of a protein derivative (chapter XXIX) called *thyroglobulin*, was first obtained in a pure form in 1915 by Professor E. C. Kendall in the United States. For many years it has been known that a deficiency of thyroid gland secretion leads to "cretinism," that is under-development, in children and to a disease known as "myxœdema" in adults; an excessive activity of the thyroid gland, however, results in what is called Graves' disease.

A provisional structure of thyroxine was first proposed by Kendall, but this was shown to be incorrect in 1926 by Dr. C. R. Harington, who later in the same year, in conjunction with Professor G. Barger of the University of Edinburgh, proved the

constitution by chemical synthesis in the laboratory. The structure was shown to be



in which it will be noted there are four iodine atoms (I) present in the molecule. Thyroxine actually contains nearly two-thirds of its weight of iodine, and people living on a diet deficient in this element are liable to suffer from the effects of defective thyroid. Synthetic thyroxine has been used for medicinal purposes and found to be as satisfactory as the substance obtained from thyroid glands; it may be noted that the laevo-rotatory form is three times as active as the form which rotates the plane of polarisation of light to the right.

An important hormone which has attracted attention in recent years is *insulin*: it is produced by glands present in the pancreas, and upon its presence in the blood stream depends the steady maintenance of the normal proportion, about 0.1 per cent, of the sugar, glucose, in the blood. If carbohydrate, that is starchy material, or sugar is consumed by the living organism, then in normal cases insulin is automatically secreted and this has the effect of causing the excess of sugar to be stored up as glycogen (animal starch) in the liver and in the muscles. When the glands do not function properly insulin is not produced in sufficient amount, sugar accumulates in the blood and the symptoms of *diabetes mellitus* ensue.

By very careful work a crystalline substance, believed to be the pure hormone insulin, has been obtained from the pancreas of animals; it has been found to belong to the group of complex substances known as proteins (chapter XXIX), and on heating it with dilute acid, that is by hydrolysis, it yields mainly a mixture of the following amino-acids: leucine, glutamic acid, cystine, tyrosine, histidine, arginine and lysine (compare p. 446). The molecular weight of insulin is very high, of the order of 35,000 in water, and hence a good many years are likely to elapse before its constitution is understood. The difficulty of the work will be realised more fully after the chapter on Proteins has been read.

A number of other secretions of ductless glands have been identified, and in recent years a great deal of attention has been devoted to the isolation of certain hormones which appear to be responsible for the physiological characteristics of male and female creatures. Three of these have been obtained in a pure form and speculations concerning their structure have been made; they all contain a complex system of carbon rings, similar to those found in the group of compounds known as "sterols," generally found associated with fats in nature, and, strangely enough, in one of the vitamins to which reference will be made shortly.

VITAMINS

At the beginning of the present century it was commonly accepted by physiologists that provided the diet of a human being or an animal contained a certain minimum of protein, obtained from meat, fish, cheese, nuts, or eggs mainly, together with sufficient carbohydrate, that is sugar and starchy materials, and fats to provide the necessary number of calories of energy, then normal bodily health could be maintained. This view was held in spite of the known fact that certain diseases, such as scurvy, at one time very common amongst sailors, and beri-beri, to which many Eastern peoples were liable, were due to a deficiency in the diet, although the exact nature of these deficiencies was by no means clear.

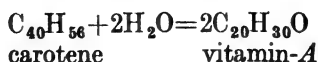
In 1906 Professor (now Sir Gowland) Hopkins, of the University of Cambridge, commenced a series of experiments to test the contention that animals could live on a diet of protein, carbohydrate and fat only, and in 1912 detailed results of this work were published which showed conclusively that certain "accessory factors," which needed only to be present in small amounts, and which contributed nothing to the energy content of the food material, were essential for normal growth and development to occur. These accessory factors are now called *vitamins*, and it is now universally accepted, that in their absence one or other of several deficiency diseases must supervene.

Since 1912 vitamins have been the subject of an enormous number of investigations in all parts of the world, both by physiologists and chemists, and at least seven of these substances have been identified. They have been named by the letters of the alphabet, approximately in the order of their identification.

Vitamin-*A* is found associated with animal fats, not with vegetable fats, and occurs especially in the livers of fishes ; the activity associated with vitamin-*A* is also found in the green parts of plants, in carrots and tomatoes. The absence of this vitamin leads to failure to grow in young animals, to an eye disease (*xerophthalmia*) in adults, and there is evidence that a reasonable supply of the vitamin protects the body from certain types of infection.

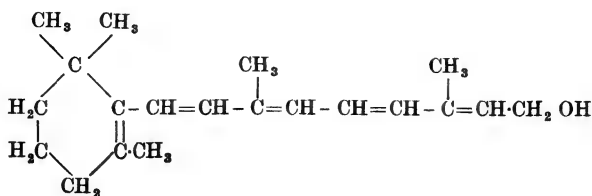
It has been known for some time that animals and fishes obtain their vitamin-*A* from green plants or from algæ, respectively, and consequently it is natural that search should have been in that direction in order to discover the identity of the vitamin. In the course of his experiments on chlorophyll, the green colouring matter of plants (see chapter XXX), Professor Willstätter found there was always associated with the chlorophyll a yellow substance now known as *carotene*. This is present in relatively large amount in the carrot, and hence the name ; it has been obtained in a pure, crystalline form and found to have the formula $C_{40}H_{56}$. Three isomeric carotenes, α , β , and γ , all having exactly the same formula, but differing slightly in the details of their constitution, have been definitely identified, and it is these substances which are converted into vitamin-*A* in the animal liver. If either of the carotenes is supplied to a living organism the physiological results are the same as those resulting from the administration of the most concentrated forms of vitamin-*A* obtained from fish livers. It was thought at one time that β -carotene was identical with the vitamin, but further work has shown this view to be incorrect ; carotene is the substance from which the animal is able to make its own vitamin-*A*, and hence the former has exactly the same effects in the living organism as does the latter. It is to carotene, consequently, that the vitamin-*A* activity of carrots, summer butter and milk is due.

The formula of vitamin-*A* is probably $C_{20}H_{30}O$, and it appears that in the liver the molecule of carotene is split into two similar parts, and a molecule of water adds itself to each part, thus :



but this reaction has not yet been achieved in the laboratory. The structure of vitamin-*A* generally favoured was proposed by

the Swiss chemist Professor Karrer ; it may be represented thus :



A remarkable point about this formula is that the left-hand portion is identical with that of β -Ionone (p. 360), which is related to the odoriferous principle of the violet, and the chain of carbon atoms attached to the ring has striking similarities to the isoprene chain in rubber (p. 376). Nature seems to work along certain definite lines, but the properties of the resulting molecules may vary considerably.

Vitamin-*B*, found chiefly in the embryo of various cereals and in yeast, was at first identified as the factor an insufficiency of which resulted in the nerve disease known as *beri-beri* ; subsequently it has been shown that there are at least three distinct substances present, and these have been called B_1 , B_2 , and B_6 . It is B_1 vitamin which is the anti-*beri-beri*, or "anti-neuritic," constituent ; this substance has been obtained in a crystalline state from rice polishings, and its formula appears to be $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_8$. A complicated provisional structure has been proposed, but it is too uncertain, as well as too complex, to be quoted here.

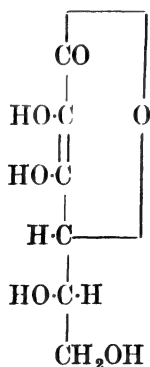
The B_2 factor appears to be responsible for promoting growth, and according to Professor R. Kuhn, of Heidelberg, it is identical with the yellow colouring matter, lactoflavin, obtained from milk-whey, which has the formula $\text{C}_{17}\text{H}_{20}\text{O}_6\text{N}_4$. The structure of lactoflavin is very complicated, but it has nevertheless been elucidated, and a synthesis has been claimed recently in 1934. Other flavins have been isolated, for example from egg-white and from various livers, and they all show some vitamin- B_2 activity.

The absence of vitamin B_6 is believed to cause in animals a skin disease resembling *pellagra* in man, but nothing is yet known of the chemical identity of this substance.

Vitamin-*C* is present in fresh vegetables and fruit, and especially in citrus fruits ; the absence of this substance is the cause of

scurvy, and so it is called the "anti-scorbutic" vitamin. It has been known for about three hundred years that lemon-juice was the best cure for scurvy, but the first definite experimental work on the subject was reported by the naval surgeon, Dr. Lind, in 1747; he showed that oranges and lemons had a remarkable curative effect in this disease, and since 1804 the provision of lemon-juice has been compulsory in the British Navy. In addition the Merchant Shipping Acts now provide that every foreign-going British ship shall carry a supply of lemon, lime or orange juice, a certain amount of which must be given to each member of the crew after the ship has been to sea for ten days.

Various attempts were made to isolate vitamin-*C* from the juice of citrus fruits, but only very minute quantities were obtained; success eventually came from an entirely unexpected direction. In 1932 Professor A. Szent-Györgyi, of the University of Szeged, Hungary, showed that it was possible to extract the vitamin in relatively large amounts in a pure crystalline form from Hungarian red pepper (paprika). A number of chemists set to work to determine the structure of this substance, and during 1933 Professor W. N. Haworth and his collaborators, of the University of Birmingham, were not only successful in this respect, but they achieved the synthesis of a substance, now called *ascorbic acid*, which has been shown to be identical with natural vitamin-*C*. This substance is related to the sugars, as will be seen by comparing its structural formula, given below, with those of some of the simple sugars shown on p. 429.



vitamin-*C* (ascorbic acid).

Ascorbic acid, like so many other substances found in nature, is optically active; the laevo-rotatory form is identical with vitamin-*C*, but the dextro-rotatory form is said to have no anti-scorbutic activity. Other derivatives of ascorbic acid, which do not occur in nature, have been synthesised in the laboratory, and several of them, having a similar arrangement of atoms to that in the laevo-ascorbic acid, have been found to have some anti-scorbutic activity, but not as great as that of ascorbic acid itself.

Vitamin-*D* is generally associated with *A* in animal fats, and is present in relatively large amounts in fish-liver oils, particularly that of the halibut; a shortage of vitamin-*D* in the diet is the cause of *rickets* and so it is often called the "anti-rachitic" vitamin. In general, shortage of vitamin-*D* leads to imperfect deposition of calcium both in bone and in teeth.

In the course of studies of rickets it was found that exposure of the body, or even certain food materials, to ultra-violet light, from a mercury-vapour lamp or from a tungsten arc, resulted in the development of the anti-rachitic factor. Search was made for the substance which gave the vitamin on exposure to ultra-violet radiation: it appeared probable, at first, that this was *cholesterol*, a substance belonging to the group of "sterols," always found together with fats and present in the fat-glands of the skin and elsewhere. Further search showed, however, that it was not the cholesterol which was the precursor of the vitamin-*D* activity, but *ergosterol*, a related substance almost invariably associated with it, first isolated from the "ergot" fungus of rye, and now obtained more readily from yeast.

By carefully controlled exposure of ergosterol to ultra-violet light about one-quarter can be converted into an isomeric form having the same formula $C_{28}H_{44}O$, known as *calciferol*; by suitable chemical means the latter can be separated out in a pure crystalline state and has been found to have intense anti-rachitic activity. The structure of ergosterol is not known with certainty, but it probably contains one five-membered and three six-membered carbon rings similar to those present in the sex-hormones previously mentioned; there are two double bonds, that is unsaturated linkages, in the ergosterol molecule, and calciferol apparently only differs from it in the position of those two bonds. Calciferol is generally identified with vitamin-*D*, although it has been suggested that there is really no proof

that this is so ; the former may happen to be a substance having the same anti-rachitic effect in the living organism as vitamin-*D* found in fish-liver oils and elsewhere. There is little doubt, however, that the two substances are closely similar if not identical.

Vitamin-*E* was first detected in 1922 ; it is present in wheat embryo and in other cereals, and also in lettuce and other green leaves. In experiments with rats it was found that in the absence of this vitamin the animals were unable to reproduce their species. The vitamin is widely distributed and minute amounts only are necessary by the body, so that a deficiency is hardly ever likely to arise. Very little serious work has been attempted on vitamin-*E* and nothing appears to be known of its chemical character.

CHAPTER XXIII

PERFUMES AND ESSENTIAL OILS

WE may now pass on to a consideration of perfumes and flavouring materials. It was among these things that one of the earliest triumphs of synthetical chemistry was celebrated when Perkin, the discoverer of the first coal-tar dye, contrived a process by which salicylic aldehyde could be transformed into *coumarin*. This was in 1868, and since a method was found in 1876 by which salicylic aldehyde could be produced from phenol, the synthesis may be regarded as complete, for, if necessary, phenol can be made from benzene, and benzene from acetylene, and the last can be formed by uniting carbon and hydrogen.

Coumarin is the fragrant substance to which the perfume of the Tonquin bean, of woodruff, and some other plants is due, and artificial coumarin is now an article of manufacture without the aid of the plant.

It was not long before a second step of the same kind was taken, for in 1876 a method was discovered for the synthesis of *vanillin*, the sweet-smelling constituent of the vanilla pod, so long used in confectionery. Here again it would be possible to proceed from the elements carbon, hydrogen, and oxygen. This, however, would necessitate several roundabout processes, and

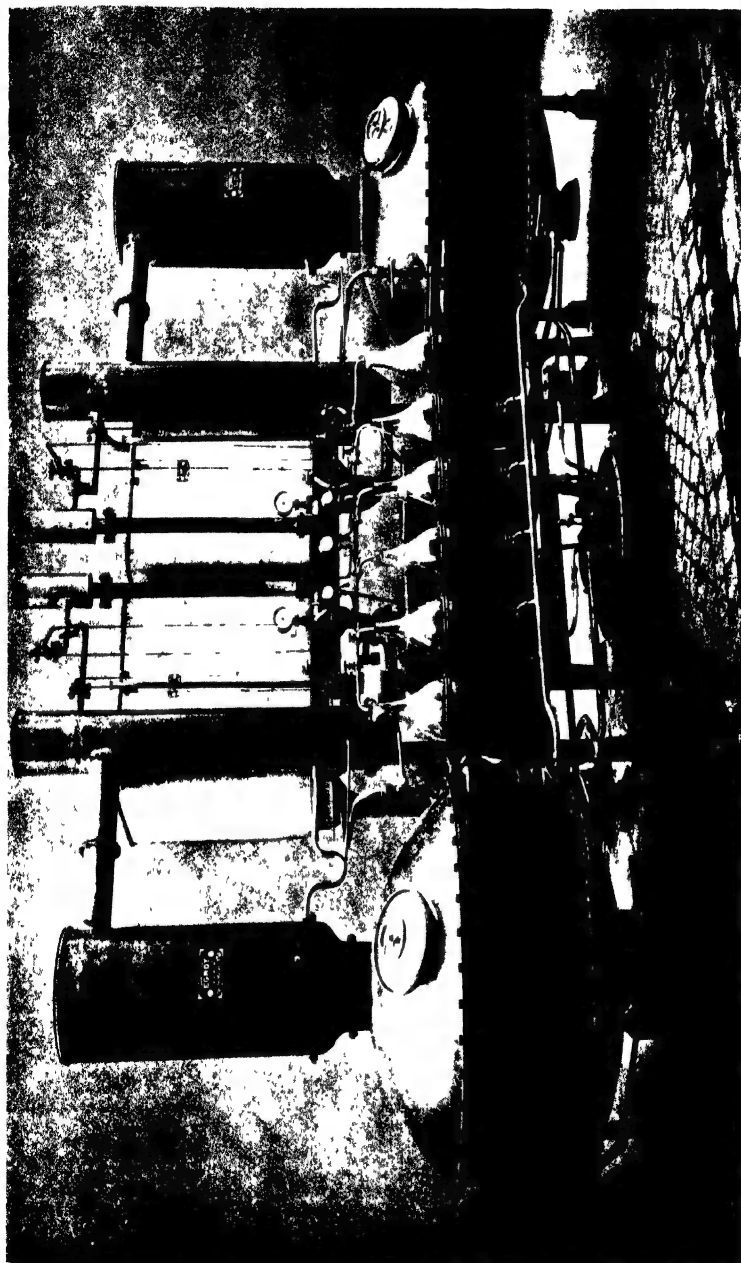


FIG. 101.—DISTILLATION OF OTTO OF ROSES IN BULGARIA



fortunately nature provides, in the substance called eugenol, a convenient and not too expensive material. Eugenol is the chief constituent of oil of cloves, and by acting on it with oxidising agents vanillin is produced.

The reader may be reminded that many years before such achievements could be placed on record the chemist had already learned that some of the fragrant essences so lavishly provided in fruit and flower and leaf could be reproduced by purely laboratory operations. As soon as organic chemistry began to be seriously studied nearly a century ago, amongst the earliest results was the production of what used to be called compound ethers,¹ by the action of various acids on common alcohol, on the alcohol from wood spirit, and on the alcohol from fusel oil separated in the rectification of whisky. Among these products were speedily recognised such odours and flavours as those of the pineapple, the jargonelle pear, and others. Pineapple owes its fragrance to ethyl butyrate, the pear to amyl acetate, winter-green (largely used in the United States) to methyl salicylate, while the strawberry and raspberry contain mixtures of several such ethereal compounds. These are now common articles of commerce.

These, however, were not alone, for already in those early days the odour developed when bitter almonds are crushed with water was found to be due to the formation of another kind of substance already mentioned in previous pages, namely, benzaldehyde. Similarly the flowers of the meadowsweet contain salicylic aldehyde, the barks of cinnamon and cassia yield cinnamic aldehyde, the hawthorn and many garden flowers secrete other characteristic aldehydes. Nor were the older chemists altogether ignorant of the constitution of the essences to which the pungency of mustard, garlic, onions, and horseradish is due. These are also ethereal salts or compound ethers which are characterised by the presence in them of sulphur associated with a radicle called *allyl* in reference to their frequent presence in plants of the genus *Allium*, belonging to the onion tribe.

The chemistry of odoriferous and flavouring materials has attracted much attention during the present century, and although the preparation of perfumes from plants is an industry which dates back many centuries, our knowledge of the com-

¹ These substances are now called "esters."

position of the "essential oils"¹ has been derived almost wholly from chemical researches conducted within living memory. Before proceeding to the most recent advances it will be in the interest of those who are quite unacquainted with the technology of the subject to explain briefly what is understood by an essential oil. An oil is usually understood to be a liquid fat which is practically insoluble in water and which floats on that liquid. When boiled with an alkaline liquid, such as solution of caustic soda, it slowly dissolves forming a solution of soap. And if a drop of oil is placed on paper it forms a translucent spot which is permanent, for common oil does not evaporate away when exposed to the air.

An essential oil is distinguished from the fatty oils first by a strong and characteristic odour; it usually floats on water, but it is slightly soluble, for the odour is commonly communicated to the water, as in such instances as the familiar rose-water or orange-flower water. An essential oil is usually changed by contact with caustic alkali, but it does not produce a soap. And lastly if a drop of essential oil is placed on paper the translucent stain disappears gradually as the oil evaporates away.

Most commonly, though not invariably, an essential oil is a mixture of two chief ingredients. One of these is a terpene—a compound of carbon and hydrogen only—the other is usually a compound of carbon and hydrogen with oxygen, and consists of an aldehyde, a ketone, a compound ether or "ester" or something else. To the latter ingredient the characteristic odour of the oil is mainly due.

Some essential oils consist of one constituent only with only slight impurities. Such, for instance, are the essential oils following:

Name of oil	Composed almost entirely of
Turpentine, American . . .	Dextro-pinene $C_{10}H_{16}$.
„ French . . .	Lævo-pinene $C_{10}H_{16}$.
Bitter almond . . .	} Benzaldehyde $C_6H_5 \cdot CHO$.
Cherry laurel leaf . . .	
Cinnamon bark . . .	} Cinnamic aldehyde
Cassia . . .	
Mustard seed . . .	Allyl isothiocyanate $SC : NC_3H_5$.
Wintergreen . . .	Methyl salicylate
	$C_6H_4(OH) \cdot C_2H_3O_2$.

¹ The significance of the adjective "essential" will be better understood when it is realised that these oils form the basis of flavouring essences and similar odoriferous substances.

The extraction of essential oils from the plants which contain them is accomplished in many cases by a process of distillation with water. The essential oil usually boils at a much higher temperature than water, but the vapour rises with the steam and both are condensed together, the oil then floating to the surface of the water from which it may be separated. The principle of the process may be easily understood by reference to the diagram.

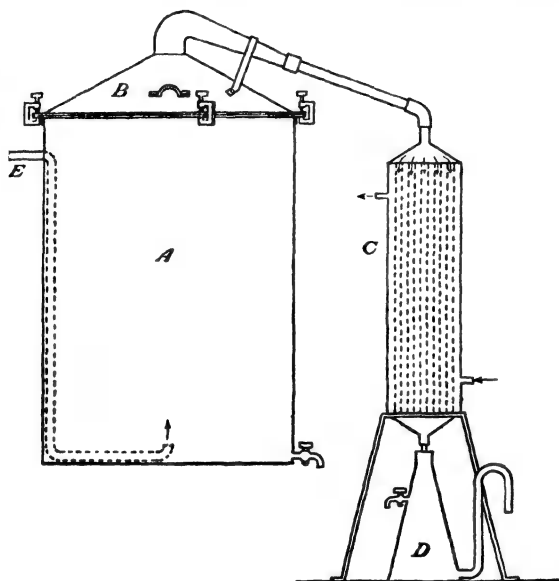


FIG. 103. DISTILLING AND CONDENSING APPARATUS

The body of the still A is generally cylindrical and is of rather large dimensions on account of the usually bulky character of the plant material to be operated on. B is the still head or cover which is usually removable. C is the condenser supplied with a stream of cold water which enters at the bottom by the pipe indicated by the arrow, and being warmed by the steam pipes within escapes at the upper pipe to the drain. D is the receiver in which both essential oil and condensed water are collected, the former remaining above in a separate layer, and the water retaining a small quantity of dissolved essence running off continuously by means of the siphon pipe into another receptacle. E shows where a pipe conveying steam may be driven into the

still so that the steam may pass through the leaves, flowers, or other matters which are supported just above by means of a wire screen resting on a frame, not shown. The condenser may consist of a number of tubes passing into a conical chamber at top and bottom as shown in the diagram,

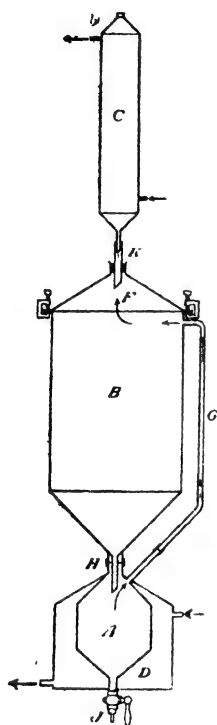


FIG. 104. CONTINUOUS EXTRACTION APPARATUS

or it may take the form of a spiral pipe coiled up in the vertical cylinder so as to be surrounded by the cooling water. This description will render intelligible some of the pictures (Figs. 101 and 102) which show several forms of still used in actual practice. In the still used for the production of otto of rose (Fig. 101) it will be seen that with a view to economy of the precious otto, the water from the receivers is returned to the stills as it comes over.

There are, however, other essential oils which cannot be extracted from the flowers or fruit containing them by a process of distillation without injury to their delicacy. In such cases as the violet, for example, the flowers are macerated in hot lard, which is afterwards pressed out retaining the perfume. The illustration (Fig. 107) which shows this process in operation at one of the factories at Grasse sufficiently explains itself. In some factories the stirring by hand is replaced by mechanical arrangements.

According to another plan, which is rapidly becoming of increasing importance, the scent may be extracted by immersing the flowers in light petroleum spirit, which can afterwards be separated and distilled off, leaving the essence behind. The accompanying diagrammatic representation of the apparatus employed in this process will render it easily understood. The percolator B is a vessel in which the flowers can be placed so that they are continuously exposed to a stream of the volatile liquid, which is driven in vapour from the receiver A up the side pipe G, and condensed again in the condenser C placed above. The arrows show the direction which the vapour takes, after it has been produced in the vessel A by the heat

applied by means of steam to the surrounding jacket or steam bath D.

The solution of the perfume is finally drawn off by the tap at the bottom of A and submitted to distillation in a separate still.

In the illustration which follows (Fig. 108, facing page 357) showing the extraction plant in practice, the percolators, etc., are shown on the right, while the recovery of the solvent is effected by means of the stills on the left.

In other cases, such as the jasmine, there is reason for believing that the flowers continue to generate and emit the perfume for some time after they have been gathered. Hence it is desirable to leave them for some time in contact with the agent, generally a solid fat, which absorbs the perfume during many days. This process of *enfleurage*, as it is called, was originally conducted by laying the flowers on the surface of a thin layer of lard spread on glass plates, renewing the flowers at intervals until the fat was duly charged. According to this plan the perfumed fat had to be melted and strained to free it from remains of petals and other impurities. Contact of the flowers with the fat has been avoided by the more modern apparatus shown in the diagram. The box is about 2 feet square and 6 feet high and is constructed so as to be practically air-tight. It is fitted with a number of glass plates, H, which are arranged so that they can be easily withdrawn and replaced. The flowers are placed on five or six trays, A, B, C, D, E, at the bottom, and beneath them are sponges or cloths, G, wetted with water. Air can be drawn in as shown by the arrows through the perforated bottom. It carries with it sufficient

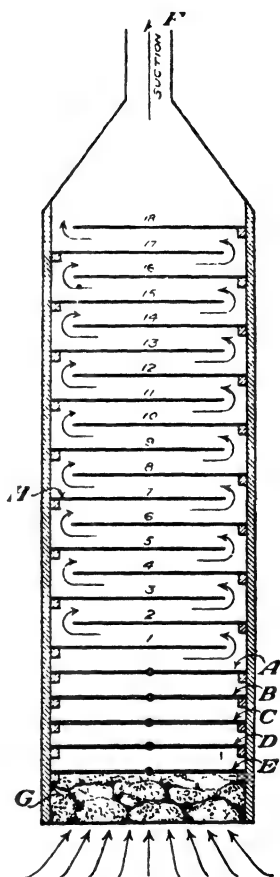


FIG. 105. APPARATUS FOR TREATING FLOWERS BY ENFLEURAGE PROCESS

moisture to prevent the flowers from drying too much, while the vapour of the perfume is carried successively over the fatty surfaces above.

By whichever method the fat is charged the perfume is extracted from it by shaking it with strong alcohol. The extract thus obtained is superior to that which is prepared by the hot maceration method previously described.

These processes are carried on in the south of France, especially at Grasse, where large quantities of flowers are grown for treatment in the factories of the neighbourhood.

In the case of the orange, lemon, bergamot, and other fruits of the orange tribe the essential oil resides in the rather large visible receptacles on the surface of the fruit. These are easily burst by pressure. If a bit of fresh orange peel is squeezed close to a flame it will be noticed that the expelled juice takes fire. The process employed in such cases consists in pricking or squeezing the rind of the fruit and collecting the oil which runs out.

The hand processes are still preferred, probably in part owing to the difficulty of inducing the Italian peasantry to change their customs. but machine pressing is rapidly growing in importance. The pricking process employs a copper saucer-shaped vessel, called an *écuelle*, the inside of which is covered with short spikes, while the oil as it exudes runs into a hollow handle inserted into the middle of the cup. In the antiquated sponge process, still largely used, the peel of the fruit is removed in thick slices, which are then pressed flat by the fingers against a piece of sponge. The oil glands are burst by the pressure and the sponge soaks up the oil, together with some juice, which is then squeezed out from time to time into a bowl, and finally filtered.

The use of perfumes is a form of luxury which in ancient times was probably limited to the rich, but in our own day they are used more or less unconsciously by everybody. For while nearly all women delight in perfumes, few men deliberately scent their persons or their clothes, but they cannot escape the use of soap, which in the form of toilet soap invariably contains some kind of essential oil. The extent to which soap is being used will be realised from the fact that in the United States and Great Britain between 20 and 23 lbs. of soap are used per head of the population each year. In Germany the consumption is only about 12 lbs., and in the eastern European countries and in



FIG 106 —GATHERING VIOLETS UNDER SHADE OF
OLIVE TREES, GRASSE



FIG 107 —PREPARING FLOWER POMADE BY HOT
MACERATION, BRUNO COURT, GRASSE

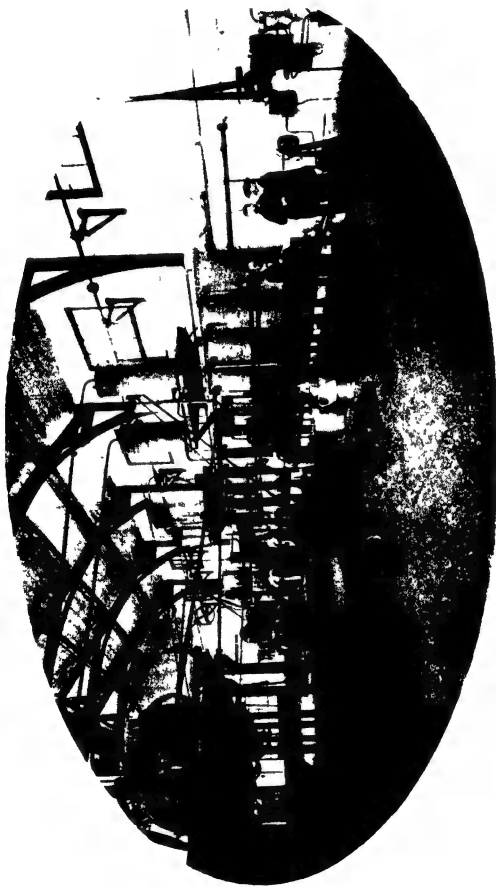


FIG 108.—MODERN FACTORY OF JEANCARD FILS & CO., LA BOCCA, NEAR CANNES
This shows the plant used for the manufacture of concrete floral essence by
extraction with petroleum ether

Asia it is still less, but is now increasing rapidly. The total annual value of toilet materials, including soaps, creams, powders, etc., has been estimated as over a hundred million pounds sterling.

The consumption of essential oils is, however, not the greatest in the form of perfume. Immense quantities are used in making drinks like lemonade and alcoholic liqueurs of all kinds, and also in confectionery and cookery. There is also an enormous demand for certain oils as medicinal agents, some for external use, others to be administered by the mouth, and many of them are included in all the pharmacopœias.

The following figures will give some idea of the magnitude of the industry connected with the production, the buying and selling of these materials.

British Trade in Essential Oils.

From	IMPORTS		
	1932.	1933.	1934.
British India . . .	£12,777	£66,667	£63,975
Other British Colonies	122,536	125,953	107,239
France	184,448	214,448	254,906
Italy	124,575	153,284	128,080
Other Countries . .	303,231	330,566	309,109
	£747,567	£890,918	£863,309
Total weight . . .	3,623,495lbs.	4,119,503lbs.	4,145,143lbs.
EXPORTS			
Value	£170,641	£167,829	£175,509
Weight	538,315lbs.	507,862lbs.	551,261lbs.

The imports and exports of essential oils by the United States are even greater ; the average value of the imports being about a million pounds per annum, and the exports approximately one-third of this sum.

France has long been a home of the industry, especially in the south, where large areas of land are devoted to the cultivation of the violet, tuberosc, jasmine, as well as orange for the sake of the flowers beside the fruit. The slopes of the Alpes Maritimes and the Basses Alpes are in many places covered with wild lavender, both *Lavandula vera* and *L. spica*. At one time portable stills, which were carried from place to place, were used for

extracting the oils, but at the present time most of the plants are collected and dealt with on a larger scale in factories.

The following data showing the amounts of various plants grown at Grasse will give some idea of the extent of the industry in France ; the figures are rough averages for recent years.

Plant.	Weight.
Orange blossoms	2200 tons.
Roses	1650 „
Jasmine	1320 „
Mimosa branches	880 „
Violets	440 „

It requires a thousand pounds of orange blossoms to yield one pound of neroli oil, and so the cost of the latter is as high as 22s. 6d. per ounce, for the best quality. The proportion of otto of roses obtained from the rose is even less ; in Bulgaria, where most of the otto is made, between seven and eight thousand tons of roses are grown annually, giving about one ton of otto. It is not surprising that the latter costs from 45s. to 65s. per ounce.

The citrus oils, such as lemon, bergamot, and orange oils are mainly produced in Sicily, the output in 1933 being 1,685,686 lbs., of which more than one-third was exported to Great Britain. These oils are much cheaper than the flower oils made in France ; Sicilian lemon oil being about 3s. 10d. per lb., and bergamot oil roughly 5s. 3d. per lb. of 37-38 per cent oil. Peppermint oil is extracted in quite large amounts both in Japan and in the United States, but this is also a relatively inexpensive oil, costing 12s. 6d. per lb. It will be noted that the flavouring oils are generally cheaper than those used in perfumery.

It is interesting to glance at the pages of one of the trade journals in which essential oils and perfumes are advertised, for there one may trace evidence of the progress made in our own time in the application of chemical knowledge, and the extent to which the artificial are now competing with the natural essences.

This synthetic industry is a development which follows naturally on the pursuit of knowledge in pure scientific chemistry without regard to possible applications. And much of the knowledge thus accumulated during the last forty years or more was no doubt regarded by the " practical " man in years gone by as useless. The story is a long one, and it would be unsuitable to a



FIG. 109.—HAULING PEPPERMINT TO DISTILLERY IN MICHIGAN, U.S.A.



FIG. 110 —INTERIOR OF IONONE DISTILLATION FACTORY
AT ARGENTEUIL, NEAR PARIS



FIG. 111 —LAVENDER FIELD IN VICTORIA, AUSTRALIA

book designed for general reading to attempt to set forth the successive steps which have led up to the position which enables the manufacturer to place on the market substances which can successfully take the place of the perfumes derived from the rose, violet, lilac, lily of the valley, heliotrope, and many other flowers.

It was feared at one time that the development of synthetic perfumes would oust the production of natural flower oils, much as artificial indigo has displaced the Indian grown product, but these fears have proved groundless. The two industries have, however, markedly assisted one another, and almost all, except the cheapest, perfumes in use at the present are mixtures of natural and synthetic products ; in this way it has been possible to obtain better scents than those given by each of the products separately. When otto of roses is extracted by steam distillation its odour is not quite the same as that of the rose, because an essential substance, known as phenyl-ethyl alcohol, is to some extent dissolved out by the water formed by the condensation of the steam. The addition of a small amount of phenyl-ethyl alcohol, made synthetically, results in a perfect imitation of the rose odour. It is not a matter for surprise, therefore, to find that large amounts of synthetic products, similar to, or identical with, those contained in essential oils, are imported and used in France ; the synthetics are made chiefly in Germany, the United States, and in England.

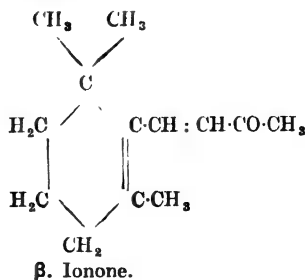
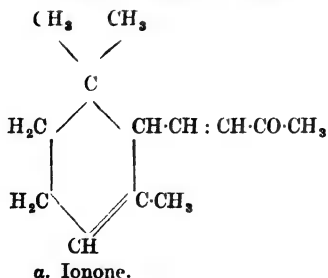
The methods by which coumarin and vanillin have been produced were described at the beginning of the chapter. To these we may now add two other examples which on account of their scientific interest as well as their commercial importance cannot be overlooked. The first of these is the substance known as *terpineol*, a crystalline solid of which there are two varieties having a pleasant odour. It is the basis of the lilac and lily of the valley artificial perfumes, and is now manufactured by the ton. The original process started with turpentine oil, $C_{10}H_{16}$, which mixed with an alcoholic solution of nitric acid is converted into a beautiful crystalline compound called terpin hydrate, $C_{10}H_{20}O_2 \cdot H_2O$. When this is distilled with water and a small quantity of almost any acid it loses the elements of water and terpineol, $C_{10}H_{18}O$, passes over in the form of a syrupy liquid. This can be crystallised by cooling. Other processes are now used.

The chemical structure of terpineol, which is a kind of alcohol, has been the subject of many researches, but it is now fully understood, as it has been produced synthetically from compounds of known constitution by the late Professor W. H. Perkin¹ in 1904.

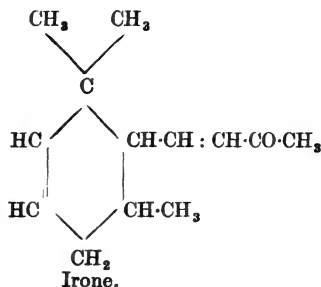
The perfume of the violet was the subject of research by Tiemann and Krüger so long ago as 1893. They found it impossible to obtain sufficient material for their work from the flowers, but as this characteristic fragrance is possessed by the dried root of iris (*orris*), the latter was used by these chemists as the source of the fragrant oil on which their experiments were made. To this substance when purified they gave the name *irone*. It belongs to the class of compounds called in chemical language ketones, and its composition is expressed by the formula $C_{13}H_{20}O$.

Protracted study of this compound led to the synthetical production of another substance to which the name *ionone* is given. This has the same ultimate composition, namely $C_{13}H_{20}O$, and closely similar properties, including especially the fragrant odour of the violet. No time was lost in applying these facts to the manufacture of artificial essence of violet. Ionone is made from citral, an aldehyde existing in considerable proportion in essences of lemon and citron, and in lemon grass oil, to which the characteristic lemon odour of these materials is due.

Citral and acetone heated together in presence of an alkali condense together to form a compound called *pseudo-ionone*, which when boiled with dilute sulphuric acid yields a mixture of two isomeric substances, α and β ionone. The relation of these compounds to one another is shown in the following constitutional formulæ, from which it will be seen that the arrangement of the atoms in each is essentially the same.



¹ For biographical note, see p. 312.



The odours of the α and β modifications of ionone are described by an expert as distinguishable by the practised nose. "The alpha-ionone is excessively sweet, having the light fragrance of the violet, whilst the beta is of a heavier type, more suitable for soap manufacture. Many of the artificial violet products sold are blends of these two bodies with natural ingredients, such as extract or oil of orris, essence of cassia, etc."

Many other perfumes are produced artificially. The following will perhaps be considered sufficient by way of example. The flowers of the May or Hawthorn (*Crataegus oxyacantha*) are believed to owe their fragrance to the presence of anisic aldehyde $\text{C}_6\text{H}_4 \cdot 1(\text{CHO}) \cdot 4(\text{OCH}_3)$, though at present direct evidence is not on record. Otto of rose is a mixture of substances of which geraniol, $\text{C}(\text{CH}_3)_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{CH}_2\text{OH}$, is the principal ingredient. It contains also another interesting compound which can be made artificially by a process which has been patented. This is phenyl-ethyl alcohol, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$, which is obtained from phenyl-acetic acid ester by reduction by sodium. It is soluble in 60 parts of water, hence, as already stated, very little remains in the otto, the greater part remaining in the rose water, which has a peculiar odour of its own.

The perfume of the hyacinth is a very peculiar one, and is supposed to be due to the presence of cinnamic alcohol, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{OH}$. This is a crystalline, though volatile, solid.

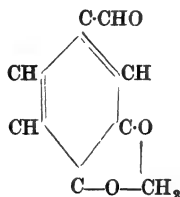
The methyl ester of anthranilic acid $\text{C}_6\text{H}_4(\text{NH}_2)\text{CO} \cdot \text{OCH}_3$ is found in neroli from orange flowers, tuberose, ylang-ylang, jasmin, gardenia, and other flowers. This also is a crystalline compound, and is made by the action of the acid on methyl alcohol in the presence of hydrogen chloride.

Methyl salicylate has already been mentioned as derived from

the wintergreen (*Gaultheria procumbens*). It occurs in a number of plants, but in most of them, including the gaultheria, it appears to exist in the form of a glucoside. The yield of oil is increased by wetting the plant and keeping it for a few hours before distillation, when a fermentation sets in by which the glucose is destroyed.

Ethyl and amyl salicylates are made and used in perfumery, but they are not known to be contained in any natural essential oils.

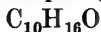
The odour of the heliotrope is said to be due to piperonal



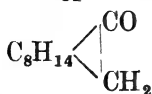
which has long been known.

The only important compound not referred to so far is camphor. This substance has been known from very early times, and before the sixth century was brought to Europe by the Arabians. In China and the East generally it has always been regarded as a valuable medicine, and is familiar enough in modern use both as a medicinal agent and antiseptic, as well as for other purposes, for example in the manufacture of celluloid. The greater part of the natural camphor of commerce is obtained from the isle of Formosa, and is distinguished as Japanese or Chinese camphor to distinguish it from Borneo camphor which is obtained from Borneo and Sumatra. The former is obtained from the *Laurus camphora*, the latter from *Dryobalanops camphora*, both large trees. Their chemical relations are indicated by the following formulæ :

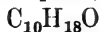
Chinese Camphor (Camphor).



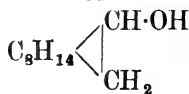
or



Borneo Camphor (Borneol).



or



Camphor has always been procured by the crude and wasteful method of cutting up the wood, in which the camphor exists in

crystals, and distilling it with water in stills of very primitive construction.

It is purified by resublimation and is obtained in large hemispherical masses called bells, or being obtained in crystalline powder is then compressed into cakes. Common camphor is a natural constituent of several essential oils, especially those of lavender, rosemary, and sage. Borneo camphor does not come into European commerce, but it is preferred in Eastern Asia, where it commands a high price, and is used chiefly for making incense and generally for ceremonial purposes.

These two substances camphor and borneol are easily converted the one into the other, having between them a difference of only two atoms of hydrogen and standing toward each other in the relation of ketone (camphor) and secondary alcohol (borneol). Hence camphor is easily made from borneol by the action of oxidising agents, nitric acid, for example, while borneol can be produced from camphor by the action of sodium on an alcoholic solution of camphor.

Camphor has been the subject of very protracted investigations, as its constitution was for many years somewhat mysterious. These difficulties have now been cleared away, and the knowledge now existing of the relation of camphor to the terpenes has enabled chemists to contrive a process by which it can be made from oil of turpentine (pinene $C_{10}H_{16}$).

The artificial camphor is identical in every respect with natural camphor, except that it is optically inactive while all the natural products rotate the polarised ray. The manufacture of camphor has been the subject of several patents, and at the present time it forms quite a large proportion of this substance in commerce. It is estimated that in a normal year about 15,000,000 lbs. of synthetic camphor are produced, mostly in Germany, as compared with, roughly, 10,000,000 lbs. of the natural product, the main source of which is Japan. About two-thirds of the total camphor is used in the manufacture of celluloid.

The history of essential oils would not be complete without at least a passing reference to the extensive class of hydrocarbons called terpenes. The most prominent and abundant of these compounds are the two pinenes which are the chief constituents of the oil or spirit of turpentine. The one obtained from the United States is known as American or as English turpentine,

and is obtained by distillation from the resinous exudation from the *Pinus australis* and *Pinus Tæda*. It rotates the polarised ray to the right. French turpentine is a similar product from *Pinus maritima*, but is lævo-rotatory. Spirit of turpentine is familiar enough as a colourless inflammable liquid with a peculiar smell. It is consumed in large quantity as a solvent and diluent in common paint, and some varnishes; as already indicated it forms the starting-point for the manufacture of synthetic camphor. It is also used as an external application in rheumatism and other disorders in which a stimulant is required.

The terpenes have been the subject of investigation in the hands of many chemists, but their constitution is now understood, and several of them have been produced synthetically since the beginning of this century.

CHAPTER XXIV

VEGETABLE FIBRE AND PRODUCTS FROM CELLULOSE

ALL plants in the earliest stages or most primitive forms are composed of *cells*, that is minute membranous bags spheroidal in form, and having no mouth or opening. As the plant reaches a more advanced stage of development these cells change in form, many assuming elongated shapes, becoming tubes often with tapering extremities. All the vegetation which clothes the surface of the earth consists therefore of a mixture of such minute hollow elements, which closely packed together form the tissues of the plant, the soft parts, as of leaf, flower, and fruit, being composed of more or less rounded cells, while the wood and veins of the leaves and other parts consist of fibres. The cells and fibres contain sap, which is water holding in solution gum, sugar, albuminous and saline matters, together with solid deposits of starch, green colouring matter (chlorophyll), crystalline solids and resinous incrustations. Now when a mass of vegetable tissue, say sawdust, has been boiled with water, with caustic soda, with alcohol, and other solvents a mass of colourless, odourless, and tasteless material remains, composed of the membrane which forms the wall of the cell and consists of *cellulose*. This is the universal basis of vegetable tissue as

already explained. Cellulose is found naturally in a nearly pure form as cotton, the hair from the seed of several species of *Gossypium*, which grows in tropical and sub-tropical climates. Examined under the microscope cotton is seen to consist of long translucent fibres more or less flattened and twisted.

In the form of cotton wool, and woven in the various cotton and linen fabrics, as well as in paper, cellulose is familiar. Cotton wool duly washed and purified may be regarded as normal cellulose. Its composition is expressed by the formula $(C_6H_{10}O_5)_n$, and as a result of recent studies of the physical and chemical properties of cellulose it appears probable that n has a value of about 200. Wood cellulose is not as pure as that obtained from cotton, and probably contains several similar compounds. Though insoluble in all ordinary neutral solvents cellulose behaves towards acids as a kind of alcohol, yielding sulphates, nitrates (gun-cotton), acetates, and benzoates when acted on by the respective acids.

There are, however, several liquids which possess the property of dissolving cellulose without obvious change of composition, so that by appropriate treatment of the solution a substance having the same composition as cellulose may be recovered in the form of a gelatinous mass. Very important practical applications of these facts have been made within comparatively recent times. Thus it has long been known that a solution of copper oxide or hydroxide in solution of ammonia will dissolve cellulose, and that when the liquid is neutralised by an acid or mixed with various other liquids the cellulose is thrown down again as a gelatinous precipitate. The solvent which is known as Schweitzer's reagent is made by immersing copper turnings in solution of ammonia and bubbling air through it. The reaction with cellulose has been turned to account in the manufacture of *Willesden Paper*, which consists of a coarse paper the surface of which is gelatinised and rendered waterproof by moistening it with the copper-ammonia solution. Within the last few years this solution of cellulose has been employed in one of the processes for the production of artificial silk, to be referred to a little later.

The action of caustic alkalis on the fibre of cotton was observed and applied about 1850 by John Mercer, a well-known calico-printer, and the product has long been known as "mercerised" cotton. The effect of the alkali is to untwist the naturally

twisted flattened tubes of which cotton fibres consist, and thicken their walls. The fabric thus treated presents a somewhat silky gloss and is increased in strength.

Another very remarkable reaction of cellulose was discovered more than forty years ago by Messrs. Cross and Bevan, well-known authorities on this department of applied chemistry.

If cellulose in any of its forms is treated with a concentrated solution of caustic soda, and the altered (mercerised) cellulose thus obtained is exposed to the action of carbon bisulphide, a yellowish mass is formed in an hour or two which swells up enormously on mixing with water and finally dissolves completely. This soluble compound appears to consist of a peculiar cellulose xanthate, to which the formula $\text{NaS}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_6\text{H}_9\text{O}_4$ has been attributed. From a solution of this compound cellulose is again precipitated by acids, by heat, or simply by long standing, in the form of a gelatinous mass appropriately termed "viscose." This also is applied to the production of artificial silk, to which reference will be made later.

Another liquid which is capable of dissolving cellulose without breaking up the molecule is a concentrated solution of zinc chloride. This solution was at one time used in the production of carbon filaments for electric glow lamps.

Strong sulphuric acid dissolves cellulose forming a mixture of sulphates, but if the acid is diluted with about half its volume of water the cellulose does not dissolve, but is superficially hydrated and gelatinised. Paper dipped into acid of this strength and subsequently washed free from the acid and dried produces *parchment* paper, a tough translucent material extensively used for a great variety of purposes.

So far only those agents have been considered which, while affecting the structure of the fibre by removing impurities or by adding to the cellulose the elements of water, do not destroy the integrity of the molecule which may be practically represented by the symbols $\text{C}_6\text{H}_{10}\text{O}_5$, though it is actually much more complex. But acids when concentrated or allowed to act for a long time are capable of breaking up this association of carbon, hydrogen and oxygen, by causing the assumption of the elements of water and a subsequent disruption of the molecule. The product is *glucose*, identical with the substance called grape sugar which is widely distributed in the vegetable kingdom. It is especially found in fruits and other sweet parts, where it is

usually accompanied by another compound called fruit sugar having the same composition, and common cane sugar. Glucose is manufactured from starch by boiling it with dilute sulphuric acid, and when the change is complete, neutralising the liquid with chalk, filtering from the gypsum formed, and then evaporating the purified and decolourised syrup in vacuum pans. Woody fibre treated in the same way also yields glucose.

The chemist has been very busy in this kind of work and especially also in the development of processes which lead up to the production of paper. We may consider in outline the preparation of cellulose fibre from the various coniferous woods growing most abundantly in Canada, Newfoundland, Sweden, Norway, and on the shores of the Baltic. The processes involved are divisible into two classes in which the details vary, but they are both applicable to other raw materials, such as esparto grass and straw. In the one case caustic soda is the agent employed, in the other a bisulphite of lime or magnesia.

According to the former method of procedure, the raw material, pine or fir wood deprived of bark, is heated with a rather strong solution of caustic soda in a boiler which bears steam pressure, and of which the contents can therefore be heated considerably above the ordinary boiling-point of water. The chemical changes which take place are very complex, but the result is that the greater part of the cellulose remains unaltered or only hydrated, while the encrusting ligno-cellulose, etc., is dissolved out. About one-third of the weight of white pine wood is left in the form of a pulp, which after washing free from soda requires to be bleached. The bleaching is effected largely by the use of so-called chloride of lime or bleaching powder, but in some of the modern processes chlorine is produced electrolytically from magnesium or sodium chloride solution in which the pulp is immersed.

In the second class of processes the acid bisulphite solution required is obtained by passing through or over a milk of lime or magnesia, the sulphur dioxide gas formed by burning sulphur or iron pyrites in suitable kilns. The wood is digested with this solution for many hours at temperatures running from 120° to 140° C. The yield of pulp is greater than in the case of the soda process, and amounts to about 40 per cent. The brownish product is then bleached as already described.

The bleached pulp, however produced, is next subjected to a process of "beating" by which the individual fibres are separated and a perfectly smooth pulp is produced. With this is incorporated the size and the various colouring matters or loading material, such as china-clay, which are required according to the quality of the paper to be manufactured. The pulp is then ready for the paper-making machine.

In all these operations there is full opportunity and need for chemical study and supervision in improvement of processes or recovery of waste products, but in a superficial sketch it is impossible to supply the details which, moreover, are to be found in the several technical treatises and dictionaries of applied chemistry to which the reader interested in these matters is referred.

For the production of the cheaper kinds of paper a large quantity of wood pulp is produced without chemicals by mechanical crushing in a stream of water which carries off the pulp as it is produced.

The importance of this branch of manufacture can be roughly estimated from the figures to be found in the official publications of the Board of Trade.

BRITISH IMPORTS				
YEAR.	PAPER-MAKING MATERIAL.		PAPER AND CARDBOARD.	
	WEIGHT. Tons	VALUE.	WEIGHT. Tons	VALUE.
1932 .	2,110,368	£9,816,000	895,785	£13,075,000
1933 .	2,222,778	£9,342,000	947,100	£12,047,000
1934 .	2,551,482	£11,113,000	1,059,250	£13,175,000
EXPORTS				
1932 .	153,976	£715,855	193,256	£6,506,000
1933 .	201,543	£907,333	187,750	£6,129,000
1934 .	231,219	£1,125,074	180,400	£6,277,000

The following data are also of interest as showing the amount of paper consumed per head of the population each year in a number of important countries representing the chief consumers ; in Great Britain and America, and probably also elsewhere, approximately one-third of the total is used for newspapers and another third for books.

ANNUAL CONSUMPTION OF PAPER PER HEAD OF POPULATION

United States of America	.	.	.	167 lbs.
Great Britain	.	.	.	81 $\frac{1}{2}$ „
Germany	.	.	.	48 $\frac{1}{2}$ „
Norway	.	.	.	39 $\frac{1}{2}$ „
Japan	.	.	.	17 $\frac{1}{2}$ „

For all ordinary textile purposes, as we have seen, the natural fibre of vegetable matter, consisting essentially of cellulose, is the basic material. It may be twisted into threads, and the threads woven by the art of the weaver into fabrics of multitudinous designs, or the fibre may be beaten by the paper-maker till it is reduced to very tiny fragments which when stirred up with water form a smooth pulp. But the fibre is still there and its structure remains fundamentally unaltered.

Cellulose may, however, be obtained in the form of continuous threads, applicable to all textile purposes, in which its natural structure completely disappears. To effect this it must be converted into a soluble substance by the action of some chemical agent, and the product is *artificial silk*. This material has no chemical connection with real silk, although it may resemble it in general superficial appearance, and so the use of the term silk is misleading; for this reason the name *rayon* has been suggested for the artificially prepared fibre.

This interesting substance belongs practically to the twentieth century, for although processes were invented and patents taken out so long ago as 1890, the use of artificial silk as a weaving material has not become commercially important till within the last few years. The remarkable progress made by the artificial silk industry is illustrated by the figures quoted below for the world production for a number of years.

Year.	WORLD PRODUCTION OF RAYON						Tons.
1896	590
1900	985
1910	7,900
1920	24,600
1930	198,000
1931	222,000
1932	230,000
1933	280,000
1934	353,000

The chief producing countries during 1934 were the United States (86,150 tons), Japan (69,300 tons), Italy (47,900 tons), Great Britain (41,700 tons), Germany (40,850 tons), and France (33,250 tons).

As a matter of history the first process employed was based on the already long known properties of the nitrocelluloses. (See also Explosives.) When cotton is immersed in a mixture of nitric and sulphuric acids with a little water, a mixture of cellulose nitrates is formed which retains the form of the cotton, but differs from it in being soluble in a mixture of alcohol and ether. The resulting viscous solution when evaporated leaves a colourless film insoluble in water, the *collodion* of the photographer. If such a viscous solution made of suitable strength is forced through minute holes or fine glass jets either into water or into a warm atmosphere, the alcohol and ether are removed and fine threads are obtained which may be wound on a spool much in the same way as in winding silk from the cocoon. The fibre thus produced, however, has the great disadvantage of being dangerously inflammable. It was therefore reduced by passing it through a solution of ammonium sulphide by which the nitrate groups it contains are removed and a substance having the composition of cellulose is reproduced. This process has survived only to a limited extent as a manufacturing process, but by the employment of other and cheaper methods artificial silk is manufactured and finds application in a variety of ways.

The cuprammonium process based on the employment of the solution of copper oxide in ammonia already described is one of these. The threads of cellulose solution are forced through jets into dilute sulphuric acid which removes the copper and reproduces the solid cellulose.

The most successful process for the manufacture of artificial silk makes use of the "viscose" method of Cross and Bevan which has been already described (p. 366); the viscous solution of xanthate is allowed to stand for some time to acquire the correct thickness (viscosity) and it is then made into fibres, as in the previous case, by forcing it through fine jets into an acid solution.

The three methods described all result in a product which is a form of cellulose, and so they are often called "regenerated celluloses," to distinguish from another type of fibre known as

“acetate silk,” or commercially as *Celanese*. This latter substance is made by treating cellulose, in the form of wood pulp or cotton, with acetic acid and acetic anhydride together with a little sulphuric acid. The product is thrown into water when it separates as white flocks; these are dissolved in acetone and the solution forced through fine orifices into hot air to produce the fibres. Cellulose acetate is also used for making films, artificial bristles and hair, and imitation tortoise-shell.

The relative extent to which the various processes are now employed is of interest: the figures show the overwhelming preponderance of viscose rayon.

WORLD PRODUCTION OF RAYON BY PROCESSES

Process.	Percentage of Total.	
	1931.	1934.
Viscose . . .	89.0	86.6
Acetate . . .	7.5	8.6
Cuprammonium . . .	2.6	4.3
Collodion . . .	0.9	0.5

It is obvious, from the brief description which has been given, that the threads of cellulose thus produced and which when spun form artificial silk, are entirely devoid of structure. Instead of being hollow, as are natural fibres, they are solid cylindrical threads, and as such present in the woven form an appearance different from that of cotton or linen. The lustre of artificial silk is greater than that of natural silk, and in the dye-bath it takes up colouring matter freely; as explained in the chapter on Dyes special dyes have to be used for acetate rayon, whereas for the other artificial silks certain cotton dyes can be used. This differentiation in behaviour to different dye-stuffs lends itself to the production of beautiful effects in cross-dyeing of union fabrics, consisting of two different types of fibres. Artificial silk has one defect and that is considerable loss of strength when wetted, which, however, is recovered on drying. Considerable improvements in the wet-strength of rayon have been made in recent years.

Further reference to cellulose products will be made in the next chapter in connection with the subject of artificial plastics.

CHAPTER XXV

RUBBER AND PLASTICS

THE substance long known as india-rubber is familiar enough, but down to a period about forty years ago the demand for it was comparatively moderate. Its use for waterproofing was known long before that time, and the great increase in the commercial application of rubber dates from the introduction of the rubber tyre as applied to bicycles and later to motor vehicles of all kinds. This increase in consumption has naturally led not only to the cultivation of the plants from which rubber is obtained, but to extensive chemical investigations into its properties and constitution which have culminated in the artificial production of what is always referred to as "synthetic rubber."

Rubber is produced by the coagulation of the *latex* or milky juice secreted by many plants. Those which yield commercial rubber flourish only in tropical or sub-tropical regions and belong to several natural orders. Of these the most important is *Hevea brasiliensis* (N.O. *Euphorbiaceæ*), which yields Para rubber, of which the amount constitutes about 98 per cent of the total rubber of commerce. Other plants of the same order are the *Manihot* and *Sapium*, which furnish a portion of the wild rubbers of Brazil.

Rubber is also obtained from different species of *Funtumia* and *Landolphia* (N.O. *Apocynaceæ*) growing in Africa.

Ficus elastica (N.O. *Urticaceæ*) is a native of India and the Malay States, which yields rubber, but less abundantly than the *Hevea*.

Down to the year 1875 no attempts had been made to provide for the demands of the rubber market artificially, and all the rubber up to that time and for some years later had been derived from the trees growing wild in the Brazilian forests. The idea of cultivating rubber plantations in the British Indian possessions was then carried into effect, and starting with large-scale experiments in Ceylon, the plantations of, chiefly, *Hevea* have extended into the neighbouring countries, more especially Malaya and the Dutch East Indies, and some other parts of the world.

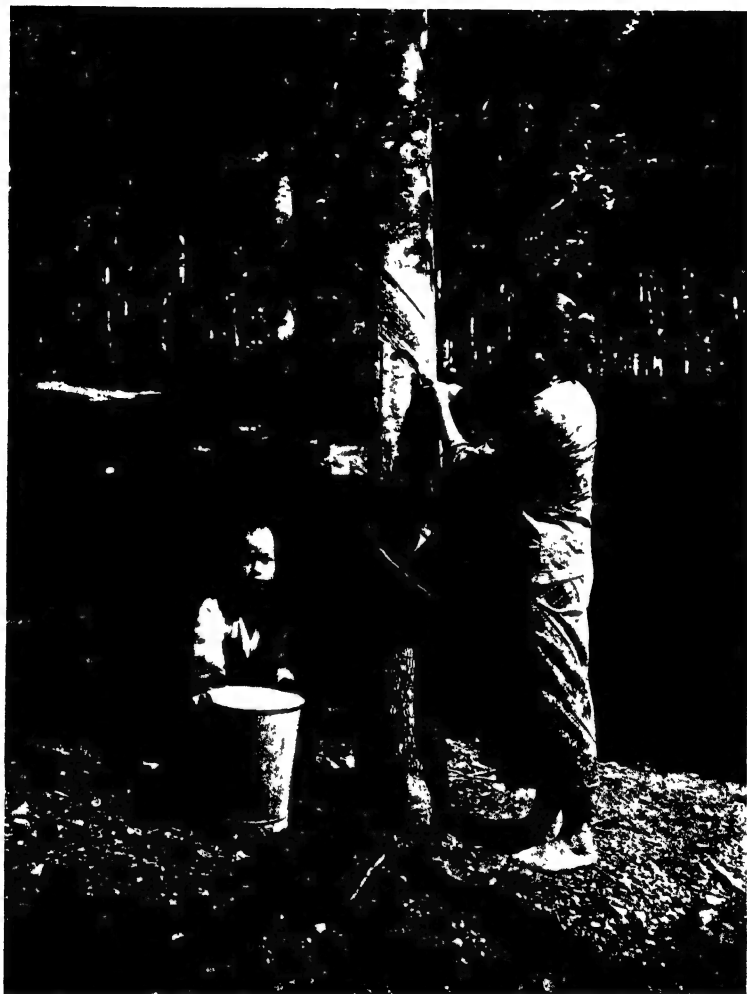


FIG. 112.—TAPPING HEVEA IN JAVA



FIG 113—YOUNG RUBBER TREES, STRAITS SETTLEMENTS



FIG 114—RUBBER AND TEA, CEYLON

The world production of rubber was 94,000 tons in 1910, but it had risen to 300,000 tons in 1919, and is now nearly three times this amount. Various estimates for the production in different countries often disagree, but the following, quoted by the Rubber Growers' Association, may be taken as a reasonably accurate average for the years 1929 to 1933.

AVERAGE WORLD PRODUCTION OF PLANTATION RUBBER
FROM 1929 TO 1933

Country.	Tons.
Malaya	434,200
Dutch East Indies	249,000
Ceylon	66,300
India and Burma	7,900
British North Borneo	6,800
Sarawak	10,000
Siam	4,500
French Indo-China	12,700
Other Countries	1,600
Total	793,000

To this amount grown in plantations must be added an average of 15,700 tons of wild rubber, mostly from Brazil ; the production of wild rubber is decreasing from year to year, although in 1910 it supplied nearly 90 per cent of the world's output. One of the chief factors in this decline is the improvements in methods of cultivation ; it is now possible to obtain from 1500 to 2000 lbs. of rubber per acre, as compared with 300 to 400 lbs. a quarter of a century ago.

The chief consuming countries and the amounts used are shown in the table below ; the figures are for the year 1933.

CONSUMPTION OF RUBBER IN 1933

Country.	Tons.
United States of America	405,700
United Kingdom	79,500
Japan	66,900
France	63,100
Germany	54,100
Russia	30,800

In the United States over 80 per cent of the rubber is employed in the manufacture of tyres and tubes for motor-cars, aeroplanes, etc. ; in Great Britain the corresponding proportion is between 70 and 75 per cent. These figures explain, of course, the amazing growth of the production of rubber since the year 1910. It is a tragic fact, however, that the fall in price has been so considerable that the total financial value of the rubber has declined ; for example, Great Britain imported 1,574,439 centals (100 lbs.) of rubber in 1913 valued at £20,524,019, but in 1934 when the importation had risen to 4,741,712 centals the value was only £11,889,510.

It has already been mentioned that rubber is obtained from the milky juice or *latex* which exudes on wounding the bark of the tree. The age at which the process of tapping should commence is about four or five years, but this is dependent on various considerations, and differs somewhat according to the kind of tree and the climate and soil of the district, which affect the rate of growth. Tapping is a process which consists in scoring the bark by means of a gouge or some kind of knife with adjustable blade, of which a large number of varieties have been patented. In the plantations a vertical channel is often cut first and a collecting tin placed at the foot. Various systems of tapping have been employed, as shown in Fig. 115, involving oblique cuts in the bark leading to the vertical channel. Latterly these have been displaced by systems involving one, or at most two, channels ; a thin strip is cut away every day, or less frequently, so as to expose fresh latex vessels (see Fig. 112).

The latex as it flows from the tree has a tendency to coagulate and to form clots or scrap which has to be dealt with separately. But the bulk of the liquid is conveyed as soon as possible to the factory, and after being strained, to remove impurities, it is mixed with a small quantity of acid, generally acetic acid. A clot soon forms which takes the shape of the containing vessel, and after washing the rubber is passed through rolls, and then dried.

The treatment of wild rubber on the Amazon is somewhat different. The latex is coagulated by exposing it to wood smoke which, of course, is accompanied by small quantities of acetic acid and vapour of creosote. In order to accomplish this the collector uses an earthen bottomless pot in which a smoky fire is made by igniting a pile of dry twigs, to which is added from

time to time the nuts of a kind of palm abundant in the district. A long wooden paddle, of which the blade is first smeared with wet clay to prevent the rubber from sticking, is then dipped in the latex and held in the smoke. A thin sheet of coagulated rubber is then almost immediately produced, and by alternately dipping in the milk and rotating the paddle over the fire, successive layers of rubber are deposited until a ball is produced of the required size, which is as much as a man can conveniently lift.

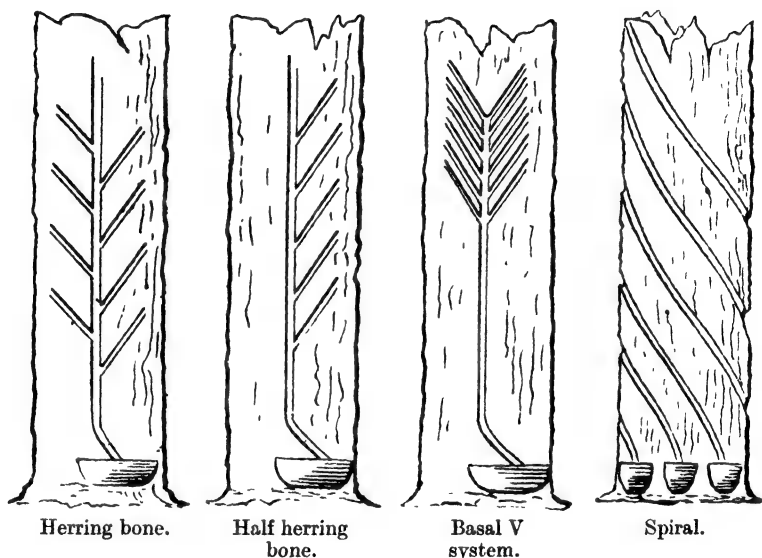
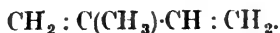


FIG. 115. VARIOUS SYSTEMS OF TAPPING

Rubber has long been known to consist essentially of a complex hydrocarbon having the ultimate composition expressed by the formula C_5H_8 . But rubber always contains larger or smaller amounts of substances containing oxygen, which for want of more knowledge are commonly called resins. Part of these resins probably result from the absorption of atmospheric oxygen by the rubber hydrocarbons. A small quantity of nitrogenous matter is also present in natural rubber, and is attributable in part to the retention of albuminous matter from the latex.

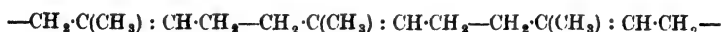
When pure rubber is heated it splits up completely into

compounds having the same percentage composition. Of these the most volatile is a liquid called *isoprene*, or methyl butadiene, the formula of which is C_5H_8 ; its structure is represented by



It boils at about 37° under atmospheric pressure, and has been the subject of much experiment in connection with the chemical synthesis of rubber. This will be referred to on a later page.

Beside isoprene rubber also yields a large proportion of dipentene $C_{10}H_{16}$ (boiling point 175°) which belongs to the series of terpenes (see Essential Oils), together with hydrocarbons of the same composition but higher molecular weight. The molecule of rubber is undoubtedly very large and complex, how large it is impossible as yet to say with certainty, but recent work indicates that the molecular weight of the rubber hydrocarbon is about 180,000, in natural rubber; this implies that there are in the molecule over 2500 groups, each having the composition C_5H_8 . The view most generally accepted is that rubber consists of a large number of isoprene units joined together in a chain, a short section of which could be represented as



The difficult solubility of rubber and its colloidal character would be consistent with such a complex formula.

Whatever the constitution of rubber may be it has one definite chemical characteristic; it contains a number of "double bonds" and so is chemically unsaturated. On this depends its power of entering into direct chemical combination with such elements as chlorine, bromine, and sulphur as well as with certain oxides of nitrogen. Its capacity for combination with sulphur and with sulphur chloride is the explanation of the important process known as "vulcanisation," upon which depend so many applications of rubber to practical purposes.

The raw rubber obtained from the latex in the manner already described is rarely used for any other purpose than for soling shoes, for almost every other application the rubber has to be treated in such a way as to increase its durability and powers of resistance, but also to give the hitherto highly plastic some permanence of form. This is achieved by vulcanisation, which involves mainly the addition of sulphur to the unsaturated mole-

cule of rubber. The rubber is masticated between rollers until it attains a soft consistency; it is then mixed with powdered sulphur, as the effective vulcanising agent, and a number of other substances, known as fillers, accelerators and antioxidants. The fillers are mineral substances, such as clay, chalk, metallic oxides, barytes, etc., according to the type of rubber required, which give solidity and toughness to the rubber, and to some extent also accelerate the vulcanising process. Originally metallic oxides were the chief accelerators, but now a number of organic compounds are known which, together with a little zinc oxide, decrease the vulcanising time from several hours to a few minutes. Most of the accelerators are sold under trade names, and only in rare cases is their nature made public; one of the best known is diphenyl-guanidine, sold under the title of D.P.G. Antioxidants, the compositions of which are kept secret, are added to prolong the life of rubber goods and to inhibit the process of "perishing" to which rubber is so liable.

The mixture is now ready for vulcanising, but before carrying out this process the plastic mass is given any desired shape; it may be made into sheets, rods, tubes or pressed into moulds. The final stage is now the heating of the articles at a temperature of 141°C ., generally by means of steam at a pressure of 40 lbs. to the square inch. The actual combination of the rubber hydrocarbon with sulphur occurs during the heating, and the final product is no longer plastic, but has a more or less rigid form. The proportion of sulphur used in vulcanisation depends on the purpose for which the rubber is required. If the amount of sulphur is relatively small, not more than one-tenth of the rubber, then the finished article is soft and elastic; with about two parts of rubber to one of sulphur the product on prolonged heating is hard, and is known as "ebonite" or "vulcanite." Its constitution is then represented approximately by $\text{C}_5\text{H}_8\text{S}$; one atom of sulphur having added itself to each isoprene unit.

For the better quality rubber goods made from thin sheet, such as mackintoshes, tobacco pouches and gloves, a cold vulcanisation process is employed; this is generally carried out by dipping the rubber sheet into a 2-3 per cent solution of sulphur chloride, S_2Cl_2 , in carbon bisulphide. In this case it is not merely the sulphur which is added on to the rubber molecule, but the chlorine as well.

What is considered to be one of the most important developments in the rubber industry of recent years is the manufacture of articles direct from latex. The difficulty of transport and the cost of carrying large quantities of water have been overcome by the addition of ammonia as a stabiliser, followed by removal of a large proportion of the water by centrifuging in a manner similar to that used for separating cream; in this way a concentrated latex, containing as much as 70 per cent of rubber, and which can be transported without coagulating, is obtained. To this latex is added the sulphur, accelerators and other ingredients required for strengthening and vulcanisation, and thin rubber articles are made by dipping moulds into the liquid so that a film adheres; the water is subsequently dried off in hot air, the temperature being generally sufficient to bring about vulcanisation, leaving an article the shape of the mould used. An alternative method of obtaining a rubber film is to make use of the electrical charge carried by the colloidal latex particles, as explained in the chapter on colloids; vulcanisation is then carried out by the sulphur chloride process.

Another new development in connection with rubber is the commercial production of chlorinated rubber, sold in England as "alloprene" and in the United States as "duroprene." Although a patent for the production of a similar material was taken out in 1859 only recently has the process become an industrial possibility. By the direct action of chlorine gas on rubber, preferably in solution, there is obtained a substance with about two-thirds of its weight of chlorine, which has been given the formula $(C_{10}H_{13}Cl_7)_n$. This chlorinated rubber is remarkably resistant to attack by acid and alkali, and forms hard and resistant non-inflammable coatings; it is being used in paints and varnishes able to resist corrosive action. Unfortunately it is not miscible with ordinary rubber, and so it cannot be used to improve the latter.

SYNTHETIC RUBBER

In the course of researches in connection with the hydrocarbons called terpenes, which include turpentine oil, Sir William Tilden¹ obtained from turpentine by the action of heat the

¹ William Augustus Tilden was born on August 15th, 1842, in St. Pancras, London; in 1857 he was apprenticed to a pharmacist for five years, and during this period he attended lectures at the School of the Pharmaceutical Society and at the Royal College of Chemistry. In 1863 Tilden was appointed demon-

hydrocarbon isoprene, which had previously been produced only by the destructive distillation of india-rubber. A peculiarity of this limpid liquid, which possesses a boiling-point close to that of common ether, is that in contact with certain reagents, common hydrochloric acid among them, it is converted partly into rubber. The liquid which remained over, after the termination of this series of experiments, was preserved in well-closed bottles. Some few years later, in May, 1892, in a paper read by Professor Tilden to the Philosophical Society of Birmingham, the following passage occurs: "I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottles contained a dense syrup in which were floating several large masses of solid, of a yellowish colour. Upon examination this turned out to be india-rubber. . . . The artificial, like natural, rubber appears to consist of two substances, one of which is more soluble in benzene or carbon bisulphide than the other. A solution of the artificial rubber leaves on evaporation a residue which agrees in all characters with a similar preparation from Para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound." At the time mentioned there was no means of further testing rubber chemically so as to establish the relation of synthetic to natural rubber, but the discovery many years later of ozonides of rubber by Professor

strator at the Pharmaceutical Society, and nine years later he became senior science master at Clifton College, then a comparatively new school; it was there he commenced his researches on terpenes. When Mason College, which became the nucleus for the University of Birmingham, was opened in 1880 Tilden was the first occupant of the Chair of Chemistry; he stayed there till 1895 when he was elected to the professorship at the Royal College of Science, a position he occupied until compelled to relinquish it by bad health in 1909. During this period the College was incorporated into the Imperial College of Science and Technology, and there were built the chemical laboratories, at that time the finest in the United Kingdom, described in the early pages of this book. On his retirement Tilden was knighted, and he devoted himself to literary work, producing four books before his death on December 11th, 1926. His most important research work dealt with the terpenes, during the course of which the artificial rubber-like substance, described in the text, was obtained. Tilden also made some comprehensive specific heat measurements, with the object of studying Dulong and Petit's relationship, and of verifying Neumann's law (p. 95). Amongst the large number of honours conferred on Sir William Tilden in his lifetime may be mentioned his election to the Royal Society in 1880, the award of its Davy Medal in 1908, and his choice as President of the Chemical Society from 1903 to 1905.

Harries of Berlin, and their decomposition products, has supplied the means of testing the identity of rubbers from different sources. This test has been applied by Professor Perkin of Oxford to Tilden's original specimens and their true character as rubber has thus been established. The remains of the original specimens examined in 1892 and exhibited at the York meeting of the British Association in 1906 have been deposited in the Victoria and Albert Science Museum at South Kensington; they are of historic interest as representing the first examples of synthetic or artificial rubber ever to be prepared.

Since these investigations much research has been undertaken on the problem. One result is that it is now recognised that other hydrocarbons presenting the peculiarity of constitution exhibited by isoprene, namely, the presence of two double linkages in the carbon chain, will also yield rubber-like substances, by a process of polymerisation, that is several simple molecules uniting to form one large complex molecule. Another wholly unexpected observation, which it was thought at one time would have an important influence on the development of a synthetic rubber industry, was made by Dr. F. E. Matthews. He found in 1910 that the hydrocarbon isoprene in contact with a small quantity of metallic sodium is converted in the course of a few hours or a few days, according to the temperature, into a mass of pure rubber. The process was of course patented. The same action of the metal was discovered soon afterwards and independently by Professor Harries. The discovery appeared to be of great value, especially as the rate of polymerisation was not interfered with by impurities, and the process could be expedited without the use of high temperatures.

About this time the demand for rubber was developing so rapidly and the price was so high, an average of nine shillings per pound throughout 1910, that naturally a great deal of attention was paid to the possibility of developing the artificial material, and much experimental work was carried out both in England and in Germany. Isoprene appeared to be the reasonable starting-point, since it has the same ultimate composition as rubber, but it was obvious that the raw material, turpentine, from which Sir William Tilden had obtained it was too expensive. In Germany, therefore, a process was worked out for obtaining isoprene from the mixture of hydrocarbons, known as pentanes, present in the low boiling-point fractions of petroleum and in

natural gas; on polymerisation this yielded the rubber-like substance already mentioned. The intermediate aimed at by the Synthetic Products Company in England was not isoprene, but the allied hydrocarbon, not containing the CH_3 (methyl) group, known as butadiene, $\text{CH}_2 : \text{CH} \cdot \text{CH} : \text{CH}_2$. The starting-point was starch, which by suitable fermentation gave a mixture of butyl alcohol and acetone, and it was from the latter that butadiene was obtained; this, under the influence of sodium, polymerised to form a substance which was, of course, not identical with natural rubber, but was thought to be superior to it in some respects.

By 1914 the price of rubber had fallen to two shillings per pound, and at this price the artificial rubber could not possibly compete with the natural article. During the war, however, when this was not available in Germany, it was essential for a synthetic product to be obtained irrespective of price, and the most successful of these was known as "methyl rubber," the intermediate stage for which was dimethyl butadiene, $\text{CH}_2 : \text{C}(\text{CH}_3) \cdot \text{C}(\text{CH}_3) : \text{CH}_2$, containing one CH_3 group more than isoprene. The starting material was acetone; it was reduced by aluminium to a substance called pinacol, and the latter on distillation lost the elements of water and gave dimethyl butadiene. The polymerisation to the rubber-like product was best brought about by allowing the liquid to stand for six to eight months at a temperature of 30° to 40° C. The methyl rubber could be vulcanised and so gave a reasonable substitute for hard rubber, such as "vulcanite" for insulating purposes, but the softer, vulcanised flexible material was quite unsatisfactory. Immediately the war ceased and plantation rubber was once more available this synthetic process was abandoned, although experimental work has been continued and quantities of synthetic rubber have been utilised in Germany from time to time.

The largely increased area under cultivation for rubber since 1921 has resulted in a fall of price, sometimes steadily and at other times cataclysmically, and in 1931 the amazingly low price of three half-pence a pound was reached; there has since been some recovery, mainly owing to production restriction schemes, but the average price in London during 1934 was about six pence per pound. At this rate it is quite impossible for artificial rubber to be regarded in the light of a competitor at present, but there is an important field for products of this type to supply

some of the deficiencies of natural rubber. The latter is not resistant to the action of oils and, in spite of many improvements, it tends to deteriorate under the influence of air and heat; varying attempts have, therefore, been made to obtain a synthetic material which can be added to ordinary rubber to improve its resistant qualities. One of these is a commercial product known as "ethanite" or "thiokol," consisting of a complex ethylene polysulphide, made by the action of ethylene dichloride on an alkaline polysulphide; it is a flexible substance with a most unpleasant odour, but it can be mixed with rubber and gives to it oil-resisting qualities, so that the mixture can be used for making flexible petrol and oil pipes.

The most important advance in the production of a useful artificial rubber-like material has come recently from America, in the form of the substance known as "duprene." In 1931 Dr. W. H. Carothers and his associates, working in the research laboratories of the great Du Pont de Nemours chemical firm in the United States, discovered¹ that the compound chloro-butadiene polymerised readily in the course of a few days to a rubber-like substance with remarkable properties. It is interesting that the difference between chloro-butadiene, $\text{CH}_2\cdot\text{C}(\text{Cl})\cdot\text{CH}:\text{CH}_2$, and isoprene, $\text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{CH}:\text{CH}_2$, is that the CH_3 group of the latter is replaced by a chlorine atom, and so the former substance is often called "chloroprene." The starting point in its preparation is the readily obtained substance acetylene; this is passed over a cuprous chloride and ammonium chloride catalyst, and under suitable conditions gives vinyl acetylene, $\text{CH}:\text{C}\cdot\text{CH}:\text{CH}_2$. The addition of hydrochloric acid (HCl) to the latter yields chloroprene, $\text{CH}_2\cdot\text{CCl}\cdot\text{CH}:\text{CH}_2$, which on standing polymerises to the complex, rubber-like substance duprene $(\text{C}_4\text{H}_5\text{Cl})_n$. In spite of its different composition duprene resembles rubber in its properties more than any other synthetic product hitherto prepared: it can be worked in exactly the same way, mixed with pigments, fillers, strengthening agents, and so on, and then made into sheets, extruded or moulded, just like natural rubber, and vulcanised by heat in the presence of a suitable catalyst, such as magnesia, *without the aid of sulphur*. The resulting product, which may be soft and elastic or hard, according to treatment, is highly resistant to heat and to the action of oils. In the past two or three years many of the

¹ See *Journal of the American Chemical Society*, 1931, p. 4203.

difficulties associated with the production and treatment of duprene have been overcome, and a supply is now available commercially; the price, early in 1935, is one dollar (about four shillings) a pound.

Duprene can be mixed with ordinary rubber with resulting improvement in properties, and it seems that, except for special purposes where cost is of secondary importance, this will prove to be the main outlet for the artificial product for the present. In order that it may be used in a manner similar to that found so useful with rubber latex, a "duprene latex" has been prepared: the chloroprene is emulsified into minute droplets with soap solution and then allowed to polymerise, so that the duprene is obtained in the form of minute colloidal particles. It is similar in properties to natural latex, but the articles made from it do not require vulcanisation. A great advance has evidently been made in the production of artificial rubber, and there are likely to be interesting developments in the near future.

PLASTICS

The term "plastics" is applied to a variety of materials of quite different compositions, which are capable of being moulded into shape by heating or by pressure, or both; the plastics of practical importance are those in which the final shape can be fixed by suitable treatment. The best known of all plastics is, of course, rubber; as already explained it can readily be made into various shapes and fixed by vulcanisation, either with or without complete loss of elasticity.

Of the natural plastics, the next important is "shellac," produced by the small insect *coccus lacca* as an incrustation on the branches of trees; it is obtained to a large extent from India and its production forms an important industry of that country. In normal years about 20,000 tons of shellac are used in Great Britain; some of this is required for the production of varnishes and sealing wax, but the larger proportion, about two-thirds, is used in the form of plastics. The most important application is to the manufacture of gramophone records; the finely powdered shellac, mixed with fillers such as china clay and other substances, is warmed and then moulded in presses. On cooling the markings produced by the moulding dies are retained. Attempts have been made to use other plastics for gramophone records, but it is

said that those in which shellac is used give least surface noise when played.

We must now turn to the consideration of artificial plastics, for these form an important branch of chemical industry that has undergone remarkable development within the past decade. The oldest, and probably best known, of all these materials is "celluloid," at one time called "xylonite"; it was obtained by Parkes, of Birmingham, and Spill, of Hackney, London, in 1856, but the first successful commercial process was worked by Messrs. Hyatt of Newark, New Jersey, in the U.S.A. In spite of competition from a variety of other products, celluloid is still the most important artificial plastic: about 90,000,000 pounds are made annually each year (1930 to 1933) in the whole world; of this amount about one-tenth is made in England and most of the remainder in the United States and in Germany.

Celluloid is manufactured by mixing well-washed and dried nitro-cellulose containing about 11 per cent of nitrogen, obtained by methods similar to those already described in the chapter on Cellulose, with about half its weight of camphor dissolved in alcohol; colouring matter and various other substances can be added at the same time. The whole mass is then rolled and worked for some time between rollers to get complete uniformity, and finally pressed into blocks. These are kept in a warm room until all the alcohol is removed, and the celluloid so obtained can either be cut or turned in a lathe, or split into thin sheets which can be moulded into various shapes whilst hot, the shape being retained on cooling.

The main disadvantage of celluloid is its great inflammability, and attempts have been made to overcome this by using cellulose acetate instead of the nitrate as the basis, but these do not appear to have been altogether successful.

Cellulose acetate, made as described in connection with artificial silk, is also used to some extent as a plastic material for moulding purposes in making fountain pens, toys, and trinkets which are non-inflammable. The acetate in the form of a dry powder is mixed with suitable fillers, colouring material and a plasticiser, which imparts a certain amount of flexibility to the product, and the mixture moulded whilst hot; thin sheets can also be pressed into special shapes which are retained on cooling. Cellulose acetate plastics become soft on warming and so materials made from it must not be brought into contact with hot water.

It may be of interest to note here that the main source of artificial silk to-day, namely viscose, was used as long ago as 1898 as a sort of plastic ; it was not actually moulded but blocks made of solid "viscoid" were turned on a lathe and made into buttons. They were, however, too expensive to have any great sale.

The most important of modern plastics is the substance known as "bakelite," named after Dr. Baekeland who first realised its potentialities ; it has been called the "material with a thousand uses," and this seems to be no exaggeration. Its excellent insulating properties, together with the ease with which it can be shaped and moulded, have made it a valuable material in many aspects of the electrical industry ; it also finds a large number of domestic applications.

In 1872 the German Professor Baeyer observed that when the coal-tar product phenol, or carbolic acid, was mixed with formaldehyde, which has been described in chapter XXII, a solid resinous material resulted, but no great importance was attached to this observation until 1908 when Dr. L. H. Baekeland, the Belgian-born chemist working in America, patented the production of this resin in the presence of an alkaline catalyst. He found that the resin when heated undergoes a remarkable change of properties : at first it softens so that it can be moulded into any desired shape, but on continued heating the material gradually hardens and eventually becomes very hard and cannot be softened again by heating. In this respect the formaldehyde-phenol plastics differ from those already described, for on reheating the latter become soft again, but the former after final hardening do not.

In the manufacture of the bakelite type of resin, the phenol or mixture of phenols and cresols, sometimes called cresylic acid (see p. 308) is warmed with formalin, that is formaldehyde solution, together with a little alkali such as caustic soda ; after some time the water is removed and according to the conditions there is left either a syrup which can be used for impregnating purposes or a solid resinous compound. The latter material ground finely, and mixed with wood flour or with fine asbestos, together with mineral fillers and colouring matters, forms the moulding powder from which all kinds of articles can be made. The powder is heated at about 140° C. and moulded in special presses : as already explained the shape acquired during the

in the form of the solid compound of formaldehyde and ammonia known as "hexamine" (p. 338), and the heating continued; the hexamine is generally added to the moulding powder and the mixture heated up in the moulding press.

The intermediate novolak resin is being used to a large extent in the new quick-drying varnishes and painting enamels; it dissolves in spirit and can also mix with the linseed oil used in paint, and on drying leaves a harder surface than that produced by natural resins. It appears that these enamels are now displacing the nitro-cellulose lacquers which had become so popular in recent years.

If the di-hydroxy-benzene, known as *resorcinol*, which is a kind of phenol obtained synthetically, is mixed with formaldehyde a vigorous reaction takes place and a resinous material results; this is rapidly self-hardening even at quite low temperatures. It is being used to some extent in the manufacture of unbreakable gramophone records, consisting of a special paper impregnated with the resinous material.

Similar in properties to the one-step bakelites are the urea-formaldehyde resins, which in England are next in importance, over a million pounds being produced each year; in the United States some five million pounds of this type of resin are manufactured per annum at the time of writing. To a mixture of urea, $\text{CO}(\text{NH}_2)_2$ (see p. 333), obtained by heating ammonia and carbon dioxide under pressure or by other methods, with about half of its weight, or less, of the sulphur analogue *thiourea*, $\text{CS}(\text{NH}_2)_2$, is added a small quantity of formaldehyde, when a syrup results. In this is soaked wood pulp or cotton linters, and the whole well masticated; after drying a material results which on grinding forms the moulding powder. Special steel moulds have to be used, as the material tends to corrode ordinary steel;

as with bakelite the plastic softens on heating and takes up any required shape into which it hardens as the heating is continued. Owing to the pale colour of the urea plastic it lends itself particularly to bright colouring, and in this respect it is much superior to bakelite. In England articles made from urea plastic are sold under the name of Beatl-ware; as it does not soften with hot water, and is more resistant to attack than bakelite, it is much used for non-fragile domestic ware.

In the United States the "glyptal" or "alkyd" resins come next in importance to bakelite, about nine million pounds being manufactured each year. These resins are made by heating together for seven hours at 180° to 200° C. a mixture of glycerin and phthalic anhydride, to which reference has been made in earlier chapters. The discovery that these substances yield a thick syrup was made by Mr. Watson Smith in 1901, at that time editor of the Journal of the Society of Chemical Industry, but the practical development of the discovery belongs to the present decade. To the syrup may be added various fillers and plasticisers, and a moulding powder that softens on warming is made from the mixture; the moulded articles harden on cooling, but re-soften on warming. Solid resins can also be obtained in the form of sheets which can be moulded like celluloid. The chief uses of the glyptal resin appear to be firstly in the manufacture of the valuable insulator "micalex," wherein powdered mica is bonded together by the glyptal syrup, and secondly in the preparation of paints, enamels, and varnishes; in these substances it forms a strong film, adhering firmly to metals, resistant to weathering and to light, and durable over a range of temperatures.

Mention must be made of the casein plastics: the first patent for the production of plastics from casein, the essential constituent of milk-curd, was taken out in the United States in 1885, but the first commercial production was in Germany in 1900 when a material known as "galalith" was made by the action of formaldehyde on casein. In common with other plastics its use has increased greatly of recent years, and it is now made in England under the names of "erinoid" and "lactoid." To the granules of casein, obtained from milk by means of rennet, are added colouring matter, a small quantity of a plasticising agent, and sometimes a suitable filling material, and the whole made into a thick paste with water; this paste is forced through heated

preliminary softening eventually becomes permanent by continued heating.

The bakelite made in the way described is called a "one-step" resin, because it goes to the completely hard stage in one heating; these must be distinguished from the "two-step" resins, which are becoming increasingly used, obtained by heating formaldehyde and phenol with an *acid* catalyst. On heating these stop at an intermediate stage, and are called "novolak" (in the United States, "albertol") resins. In order to complete the hardening more formaldehyde and some alkali must be added, generally in the form of the solid compound of formaldehyde and ammonia known as "hexamine" (p. 338), and the heating continued; the hexamine is generally added to the moulding powder and the mixture heated up in the moulding press.

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nozzles in the form of rods, tubes, and strips. If sheets are required the strips are either flattened out by pressure whilst heated, or else they are forced together by heat and pressure into a block from which thin slices may be cut by means of a special planing machine. The casein material is now immersed in a 5 per cent formalin bath for some time to harden ; it is finally removed and dried in hot air. In this final form the plastic can either be turned or drilled on a lathe, or it can be softened in hot water and so moulded or stamped. The casein plastics can be produced in a remarkably beautiful range of colours, and the material takes a high polish ; it is used specially for buttons, but there are many other applications, such as for fountain pens, pencils, small electrical parts, knife handles, and imitation tortoise shell. As it softens in hot water the casein plastics cannot be used for domestic utensils.

The "solvent naphtha" fraction obtained from coal-tar distillation contains a number of substances for which little use was found until recently. Amongst these may be mentioned particularly the related compounds *coumarone* and *indene*, which distil over between 168° and 182° C. ; it has been known for over forty years that if to these substances is added a small quantity of concentrated acid a polymerisation process occurs, that is to say several simple molecules unite to form a large, complex molecule, and the product is a resinous substance now known as "coumarone resin" or "cumar." This material dissolves in hot linseed oil as well as in spirit, and on drying leaves a very hard film ; it is consequently replacing copal gum and shellac in the paint industry. In the United States cumar resin is also used in the manufacture of "chewing gum."

In addition to the synthetic plastics and resins already mentioned others of minor importance, at the moment, are being made commercially or are being tried out experimentally. Of these mention may be made of benzyl cellulose, still another derivative of cellulose to find industrial application. Before closing this chapter, however, it will be of interest to give some idea of the extent of the artificial plastics industry, apart from the production of celluloid which does not really belong to the present century. In 1923 there were produced in Great Britain about a million pounds weight of phenol-formaldehyde resins, but in 1933 the amount had increased tenfold ; in the United States the corresponding figures are 11,000,000 lbs. in 1923, and

31,000,000 lbs. in 1933, the latter amount being below the record production of 34,000,000 lbs. in 1931. Although the bakelite type of resin represents the greatest proportion the others are also made in considerable quantities, and some figures of production have been already given. It will be seen that in the manufacture of artificial plastics a vast industry has arisen from a few apparently unimportant and trivial observations made generally before the present century. For the reader who wishes further information on the subject of plastics the special journals, such as *British Plastics*, as well as text-books on the subject, should be consulted.

CHAPTER XXVI

EXPLOSIVES

“ . . . it was great pity, so it was,
This villainous saltpetre should be digg'd
Out of the bowels of the harmless earth,
Which many a good tall fellow had destroy'd
So cowardly ; and, but for these vile guns
He would himself have been a soldier.”

WHEN Shakespeare put these words into the mouth of Hotspur the only use for gunpowder was in the practice of war, and for purposes of destruction such as was contemplated in the Gunpowder Plot of 1605. But though the mention of explosives immediately suggests war, it must not be forgotten that these agents have been among the most powerful auxiliaries in the arts of peace. It is only necessary to consider how many roads, railways, tunnels, and water works have been rendered possible by the use of dynamite and other blasting materials to perceive that explosives have a civilising mission of their own, and probably next to steam have done more to facilitate inter-communication between different countries than any other of the works of man's invention. The importance of explosives to industry will be realised when it is remembered that nearly half a million tons are used in the world each year in times of peace.

The chemist of the twentieth century is acquainted with a large number of substances which when heated or struck or in some cases even merely shaken explode, but the great majority of them are useless for practical purposes, being too unstable to

be handled or carried about without great danger to the person. By an explosion the chemist understands the sudden production of a relatively large volume of a gas or gases from a solid, liquid, or mixture of gases. And as such changes are almost always attended by the production of much heat, the hot gases formed are still further expanded. For the moment the last case must be postponed from consideration, but the reader will easily understand what is referred to by thinking of the disastrous effect in a coal-pit when a mixture of air with inflammable gas from the coal, called *fire-damp*, comes into contact with a flame. The resulting explosion which, under such circumstances, does nothing but mischief, can in another form be turned to useful practical account when under control in the gas-engine or internal combustion engine of the motor.

But although explosive substances are familiar in the chemical laboratory, and have multiplied among the products of modern chemical research, it is curious to note that nearly all the explosives employed as propellants or for blasting purposes are produced more or less directly by the use of the "villainous saltpetre" so long an ingredient in old-fashioned black gunpowder. The object in all cases is to introduce into a mixture or compound containing the combustible elements, carbon and hydrogen, so large a quantity of oxygen that the product will burn without the assistance of atmospheric air.

This is effected in the case of gunpowder through the agency of the nitre or saltpetre which supplies oxygen to the sulphur and charcoal with which it is mixed. Or it may be by bringing cotton or glycerine or phenol or some other compound of this kind into contact with nitric acid. An interchange is then effected whereby a portion of the hydrogen of the original substance is removed in the form of water and a group of atoms characteristic of the nitrates is introduced. When the nitrated compound is fired the oxygen combines with carbon forming gaseous oxides of carbon, and with the hydrogen forming water, which is of course liberated in the form of steam, while the nitrogen is set free in the state of gas and thus contributes to the total volume of gas formed in the act of explosion.

This chapter must be devoted to an account of the chemical composition and action of the modern explosives, some of them of quite recent introduction, but to understand why some of the changes which have taken place of late years have been intro-

duced, it is necessary in passing to glance at the changes which have taken place in the construction of military and naval guns.

At the time of the Crimean War the largest guns ashore or afloat were the 68-pounders with smooth bores. The idea of rifling the gun for the purpose of giving the projectile the spin which increases greatly its accuracy of fire had not at this time been actually adopted in practice. With this very important change two names will always be connected, the late Lord Armstrong (died 1900) and the late Sir Andrew Noble (died 1915), who for some forty years were associated together in the great Elswick Ordnance Works near Newcastle-on-Tyne. To the former we owe the rifled breech-loading gun with wire-wound cylinder, to the latter the invention of the chronoscope, by which minute fractions of time may be measured, beside famous experiments on the pressures attained in large guns.

Up to about 1886 black gunpowder had been used, but as it had been found that with increased length of the gun the pressure on the breech became injurious to the gun without giving the desired velocity to the projectile, many modifications were tried in the size of the grain, and in the cubes, prisms or perforated slabs in which form the powder was used. The old powder, however, had one inseparable defect, namely, the large quantity of smoke produced in firing. This arises from the fact that black gunpowder is composed of nitre, charcoal, and sulphur in the proportions on the average of 75 : 15 : 10 per cent respectively. Hence when burnt the potassium of the nitre is converted into a mixture of potassium carbonate, potassium sulphate, with a small quantity of potassium sulphide, all of which are solids, and being dispersed in fine powder give rise to clouds of smoke. At the time referred to the service powders used by the various European Powers had the composition shown in the following table :

Country.	Nitre.	Charcoal.	Sulphur.
England Black Powder	75	15	10
„ Brown „	79	18	3
Sweden	75	15	10
Russia	75	15	10
Prussia	74	16	10
Saxony	74	16	10
United States	76	14	10
Austria	75·5	14·5	10
France	75	12·5	12·5

According to Thorpe's *Dictionary of Applied Chemistry* Chinese gunpowder contained nitre 61.5, charcoal 23, and sulphur 15.5 parts per cent. This departure from the type, which has been established by modern scientific methods of manufacture, is interesting when the tradition is recalled which attributed the invention of gunpowder to the Chinese.¹

Changes in the guns then demanded changes in the rate of combustion of the powder used in them, while the conditions of modern warfare required a propellant which should be practically smokeless. It seemed useless to construct quick-firing guns and machine guns capable of delivering a shower of bullets if after the first discharge or two all view of the enemy in front of the guns became impossible. Gun-cotton, which is the essential basis of all modern propellants, differs from the old powder in yielding only gaseous products in its explosion, without any solid and hence without smoke. There is also an important difference between the two, in the fact that the old powder is merely a mechanical mixture of solid ingredients, the particles of which, under a microscope, can be seen lying side by side but quite distinct from one another, while gun-cotton is a chemical compound. In the former, therefore, the oxygen required to combine with the sulphur and with the carbon of the charcoal has to be liberated first from the particles of the nitrate and then to attack separately the particles of the combustible sulphur and carbon.

In gun-cotton and similar substances, each molecule of the compound contains within itself the elements which are to combine together to form the gaseous products of the explosion.

This will be understood by reference to the equation given below.

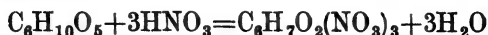
As already stated in an earlier chapter, clean cotton consists of almost pure cellulose, which has the formula $(C_6H_{10}O_5)_n$,

¹ The invention of gunpowder is by the English attributed to Roger Bacon, who was born in 1214. Others suppose a certain monk, of whom nothing positive is known, but who is supposed to have lived in the early part of the fourteenth century, to have been the inventor. He is commonly spoken of as Berthold Schwarz, a purely imaginary name.

Gunpowder and cannon were known to have been used in England in 1344, in France in 1338, and the Oxford MS. "De officiis regum," dated 1325, gives an illustration of a gun. The invention of gunpowder must therefore be placed at an earlier date.

Those who are interested in the history of the subject should consult *Monumenta Pulveris Pyrii*, by the late Oscar Guttman, 1906.

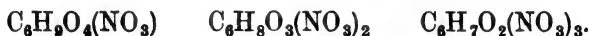
where n is a large number ; there is in addition a small amount of mineral matter, as may be seen from the ash left when the cotton is burnt away. When cotton is immersed in strong nitric acid an interchange takes place which may be expressed by the following equation :



in which it is obvious that the product is a nitrate, and its formation is comparable with the production of a nitrate when caustic potash is mixed with nitric acid. Water is in both cases formed simultaneously :



In the case of cellulose three stages of nitration are possible, the products being represented by formulæ, thus :



Gun-cotton or nitrocellulose, which should more strictly be called cellulose nitrate, consists mainly of the last of these three substances, the trinitrate.

It has long been known that when starch, paper, cotton fibre, or other vegetable material is soaked in very strong nitric acid and is subsequently washed in water and dried, the cotton or other material is scarcely changed in appearance, but it is found to have increased in weight, 1 part of cotton giving, according to the theory explained above, 1.8 parts of nitrated cotton. This material is extremely inflammable, and on contact with a flame disappears instantaneously with a bright flash. The Swiss chemist Schönbein, so long ago as 1845, proposed to use this product as a substitute for gunpowder. It was, however, many years before the manufacture of gun-cotton could be carried on without danger of explosion, and before the product could be obtained in a condition in which it could be stored and used for any purpose with reasonable safety. A long series of experiments, conducted first by the Austrian General von Lenk, and later by Sir Frederick Abel in this country, led to the discovery of the conditions necessary for this object, the first essential being the removal of the last traces of acid from the nitrated cotton.

At the present day gun-cotton as well as nitroglycerine, to be described later, is manufactured in large quantities in many

countries in which the regulations controlling the operations vary. In the United Kingdom the Explosives Department of the Home Office prescribes the conditions which must be obeyed.

In laying out explosives works it is necessary to distinguish the danger area from the non-danger area. In the latter, boilers, engines, acid stores, and other departments may be arranged in any manner found to be most convenient, but in the former where the manufacture of the explosive is carried out the case is quite different. Restrictions are imposed in order to prevent the introduction of any materials likely to set off the explosive material. The buildings are so arranged as to allow only limited quantities of explosive material and a limited number of work-people in one building at a time, and further to place the different buildings at such distances from each other, or surround them by protecting earth mounds (Fig. 116), that in the event of an explosion the amount of damage and loss of life is reduced to a minimum.

The manufacture of gun-cotton and the other forms of nitro-cellulose is carried out in the first stages in the non-danger part of the factory. The raw material is cotton waste, which is specially prepared for the explosive manufacturer. First it is hand picked in order to remove all foreign matter as much as possible, and it is amazing to see how much rubbish in the form of pieces of wire, wood, nails, etc., is thus removed. Next it is teased and dried, because cotton ordinarily contains about 10 per cent of moisture and this water would needlessly dilute the nitrating acids. The photograph (Fig. 118) shows a drying-plant in use at Waltham Abbey. Here it is exposed to a temperature of about 80° C. for twenty minutes. It is then weighed up, according to the older method introduced by Sir Frederick Abel, into lots of 1½ lb. called a charge, and is kept dry in an air-tight box till it is dipped.

The acids used consist of a mixture of 1 part by weight of strong nitric acid of specific gravity 1.5, with 3 parts by weight of strong sulphuric acid of specific gravity 1.84. Mixing the acids is attended by evolution of heat and the mixture is allowed to become completely cool before it is run into the cast-iron dipping tank.

The charges of cotton are immersed in the acid for a few minutes, then placed on a grating and the excess of acid squeezed out. The partially changed cotton, still saturated with acid, is



FIG. 116.—MOUNDED HOUSE, COTTON POWDER WORKS



FIG. 117.—BUILDINGS AND PIPE CONNECTIONS
COTTON POWDER WORKS

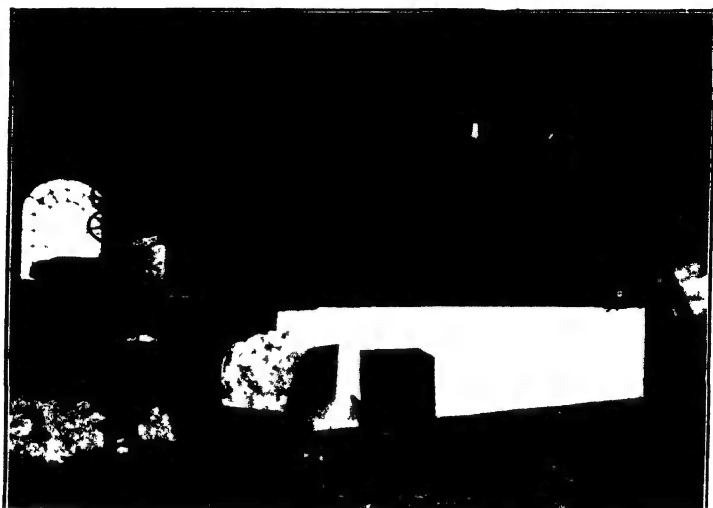


FIG 118 — DRYING MACHINE, WALTHAM ABBEY



FIG 119 — ABEL NITRATION PROCESS. DIPPING PANS
WALTHAM ABBEY

placed in an earthenware covered pot standing in water, and left for about twelve hours (Fig. 119). The nitration is then complete, and the contents of the pots are lifted out by tongs and placed in a centrifugal machine, where the excess of acid is wrung out. The gun-cotton is then placed in a tank full of running water till the water no longer answers to a test for acid.

To remove the last traces of acid the cotton requires to be boiled with water repeatedly. It is then reduced to pulp which, suspended in water, is passed by a pipe into the "poaching" machine, where paddles keep the fine pulp agitated with water and thoroughly wash every portion of it. After some hours a small quantity of lime-water, whiting, and caustic soda is added so as to leave the cotton pulp slightly alkaline. It is then drawn off by means of a vacuum pump, and the pulp strained off in measured quantities into moulds, where pressure is applied sufficient to reduce the substance to the condition of a solid cake hard enough to bear handling. Finally, the moulded cotton is submitted to hydraulic pressure amounting to about five tons on the square inch, which leaves the cake so hard that it does not yield perceptibly to pressure by the finger.

Newer methods of nitration have been introduced by which a larger quantity of cotton can be immersed in the acids at one time.

Centrifugal machines have been constructed which can be filled with the acids and a much larger weight of cotton, generally about 17 lbs., can be immersed. When the nitration is complete the acid can be run off and the cotton drained by setting the machine in motion.

Another method employed at the Royal Factory, Waltham Abbey, is known as the displacement process. The plant consists of shallow earthenware circular pans grouped together in sets of four. They are provided with perforated false bottoms, and the bottom of each pan is connected with a pipe by which the nitrating acid can be supplied, and a pipe by which the spent acid can be drawn off. These pans will each take a charge of 20 lbs. of dry cotton.

When all the cotton is immersed perforated earthenware plates are laid on top of the cotton to keep it under the acid, and a thin layer of water is cautiously run over the surface which prevents the escape of acid fumes. After two and a half hours the nitration is complete; the spent acid can be drawn off, and an

equivalent quantity of water run into each pan. In this way the spent acid is displaced much more completely than by the older methods.

After draining off the water from the pans the gun-cotton is ready for the processes of purification already described.

In some factories a continuous process for nitrating cellulose is used ; the latter is formed into a continuous band and passed at the appropriate speed through the bath of nitrating acid, so as to give the desired extent of nitration. Fresh acid is added to the bath continuously in order to maintain its concentration. The nitrated cellulose is then washed carefully to remove excess of acid.

Up to this point the nitrated cotton has been treated as non-explosive, but in order to dry it, it is removed to one of the stoves in the danger area. Dry gun-cotton is one of the most dangerous explosives, as when dry and warm it is very liable to explode by friction, and the greatest care has to be exercised in handling it.

In the production of gun-cotton the composition of the acid mixture is of the utmost importance, and if the sulphuric acid present is deficient in amount, or the proportion of water formed in the process is allowed to exceed a certain amount the nitration does not reach the maximum. Nitrocellulose having the composition expressed by the formula given above contains just over 14 per cent of nitrogen. Gun-cotton, however, usually contains somewhat less than this percentage, namely, about 13·3 per cent, owing probably to the presence of small quantities of one of the lower nitrates, the formula of which has already been given.

Generally speaking, the lower nitrates are soluble in a mixture of ether and alcohol, while gun-cotton is not dissolved by this liquid.

Gun-cotton requires a lower temperature than gunpowder for its ignition. The rate at which it burns depends on the mode of ignition and the conditions under which it is fired. A mass of loose gun-cotton may be ignited on the open hand without burning the skin or producing more than a momentary sensation of warmth, while the same cotton lightly twisted would produce a burn, and if confined in any sort of strong envelope would explode. The difference consists in the rate at which decomposition is transmitted through the mass, and the discovery that the explosion of a detonating fuse containing fulminate of mercury

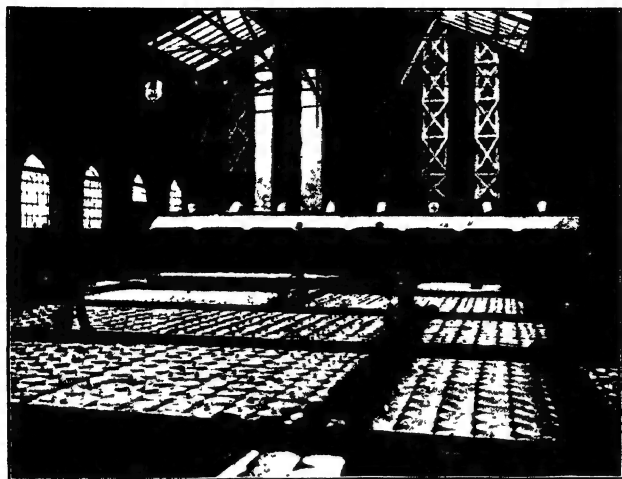


FIG 120 —ABEL NITRATION PROCESS, WALTHAM ABBEY



FIG 121 —BEATING ENGINES AND POACHER
WALTHAM ABBEY



FIG 122 —DISPLACEMENT PROCESS, WALTHAM ABBEY

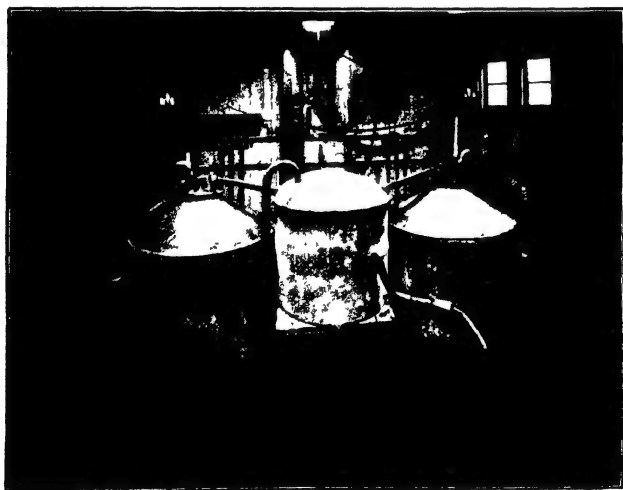


FIG. 123.—NITRATOR-SEPARATORS

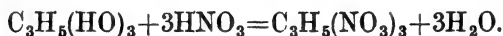
or some similar compound in contact with a mass of gun-cotton would cause it also to explode was a step of great practical importance.

Nitroglycerine, a compound similar in constitution to nitro-cellulose, both being nitrates, was discovered by Sobrero, an Italian chemist, in 1847. Though its explosive properties were known it was regarded as dangerous, and was not generally used as a blasting agent till after 1867 when Alfred Nobel discovered a method of rendering it portable and less dangerous by incorporating the liquid with a sufficient quantity of a fine silicious earth, called kieselguhr. The product is dynamite, which is familiar enough by name to the public.

Nitroglycerine is produced very simply by the interaction of a mixture of nitric and sulphuric acid with pure glycerine.

Glycerine is the secondary product obtained in boiling fat or oil with caustic alkali for the purpose of producing soap. But a large quantity is also produced by distilling fats in super-heated steam, when the fatty acid and glycerine are obtained, and it is only necessary to evaporate the watery part of the distillate to obtain the glycerine.

Glycerine, or glycerol as it is called in systematic chemical language, is a familiar colourless syrupy liquid, with a sweet taste. When mixed with nitric acid under suitable conditions it is converted into nitroglycerine, more correctly called glyceryl nitrate, and at the same time water is produced :



While formerly only small quantities at one time of glycerine were acted on by the acids, a charge of 1400 lbs. of glycerine may be now used in one operation in the apparatus called a nitrator-separator. In the modern practice a mixture of strong nitric acid and sulphuric acid is used, together with a certain amount of anhydrous sulphuric acid in the form of what is called *oleum*, which combines with a larger proportion of water, with the result that the yield of nitroglycerine is not far short of the theoretically possible amount. From the formulæ 100 parts of glycerine should yield 246.7 parts of the nitrate, while in practice upwards of 230 parts are obtained.

The nitrator-separator is a cylindrical leaden vessel with a coned top; inside are pipes through which compressed air is blown to mix the contents. The glycerine is introduced in the

form of a fine spray under the acid by means of a special injector worked also by compressed air. In order to avoid the possibility of accidents precautions are taken to see that the temperature does not rise beyond a certain point, generally 28°C . By reducing the flow of the glycerine and by increasing the agitation with the air any undue tendency to rise can usually be checked.

When everything goes right the nitration of the charge is usually completed in about one hour, the agitation with the air is discontinued, and the separation of the nitroglycerine from the acids takes place; being lighter it comes to the top. The nitroglycerine is forced out into a washing tank where it is stirred up repeatedly with fresh water, then with a solution of sodium carbonate, and finally with water. After this it is filtered to remove traces of water or impurities.

Nitroglycerine is a colourless oil of specific gravity 1.6, and therefore sinks in water in which it is insoluble. It has a sweetish taste and is poisonous. In minute doses it is used in medicine. When a lighted match is applied it burns quietly away, but it detonates violently when struck on an anvil by a hammer or by sudden heating to 257°C . Nitroglycerine becomes solid when exposed to frost, and in use it requires to be thawed, an operation attended by considerable risk. "Non-freeze" varieties of nitroglycerine are generally obtained by the addition of a small amount of the nitrate of a substance known as glycol, which is related to glycerine in composition.

In 1875 it was discovered by Alfred Nobel that when a low grade of gun-cotton and nitroglycerine are mixed together the cotton loses its fibrous or cellular structure and becomes gelatinised. In the product each constituent has its explosive properties modified, and the mass becomes better suited to blasting purposes than either ingredient separately. This substance has been largely used under the name "blasting gelatine," and it is otherwise interesting as the forerunner of the various mixtures which have been the subject of experiment and which have resulted in the production of the chief military propellant *cordite*. It was discovered that not only could the lower nitro-celluloses be gelatinised by nitroglycerine, but that the most highly nitrated cotton could be blended with nitroglycerine if the mixture was treated with a common solvent such as acetone.

To manufacture cordite the nitroglycerine is poured on to the gun-cotton contained in rubber bags and hand-mixed. The paste produced is then transferred to a large Pfeleiderer mixing machine, similar to the machine used in some bakeries for mixing dough, and the requisite quantity of acetone added. After working the mixer for some time, 5 per cent of vaseline is added to increase the stability of the product and lubricate the gun. When gelatinisation is complete the mass is pressed through a die of the requisite size, and the *cord* which is thus formed wound on a reel, or in the case of the thicker sizes it is cut into suitable lengths. The cordite is then dried slowly to drive off the last traces of acetone. In the case of the larger sticks, containing the smaller quantity of nitroglycerine, 30 per cent, this drying takes about two months.

The most important high explosives for use in shells are picric acid and trinitrotoluene, these are both obtained by acting on one or other of the constituents of coal-tar (see chapter XX, p. 308) with strong nitric acid.

In the manufacture of picric acid phenol, or carboic acid, is mixed first with about five times its weight of sulphuric acid when a compound known as phenol-sulphonic acid is formed. Strong nitric acid is then added gradually to the mixture, when trinitro-phenol, or picric acid, is produced in the form of lemon yellow crystals. The latter are removed and washed well to remove adherent nitric and sulphuric acids. Picric acid was at one time in common use as a dye for silk and wool, and is still employed medicinally for the treatment of burns. It melts at $122^{\circ}\cdot5$ C., and is a moderately strong acid, forming a variety of salts called picrates with metals.

Many of the picrates explode when heated or struck, but picric acid burns quietly. When the fused acid is supplied with a detonator it explodes violently, and it has been largely used under the name lyddite, or melinite, for charging shells. Experience has shown that lyddite shells are, however, somewhat erratic.

Trinitrotoluene, T.N.T., is found to be more trustworthy, and though its explosive force is somewhat less than that of picric acid it is preferred on account of its stability, and being not an acid but perfectly neutral it is not liable to attack the surface of metals.

Toluene is a colourless liquid which by the action of

strong nitric acid is converted successively into three nitro-compounds :

C_7H_8	toluene
$C_7H_7NO_2$	mononitrotoluene
$C_7H_6(NO_2)_2$	dinitrotoluene
$C_7H_5(NO_2)_3$	trinitrotoluene or T.N.T.

The toluene is first nitrated to produce mononitrotoluene ; this and strong sulphuric acid are then fed in at opposite ends of a series of pots, nitric acid being added at intermediate stages. The completely nitrated T.N.T. issues as an oil at one end of the series and spent acid at the other. The liquid T.N.T. is allowed to solidify on cooling and is then purified, generally by washing it with a solution of sodium sulphite which dissolves out most of the impurities.

Trinitrotoluene is a yellowish crystalline powder with a melting point about 80° C. When detonated by mercuric fulminate it explodes with great violence giving a quantity of black smoke, whence some of the names—Black Maria or Coal Box—given by the soldiers to shells of this kind.

T.N.T. is sometimes mixed with other substances, especially with an oxidising compound such as ammonium nitrate, together with a little aluminium powder and a trace of charcoal, the mixture being known as ammonal.

Other constituents of coal-tar yield explosive compounds under the action of nitric acid.

Dinitrobenzene, for example, enters into the composition of the mining explosives roburite and bellite. Trinitrocresol has been used in place of picric acid under the name ecrasite, but it shares the disadvantages of picric acid.

Cheddite is a name given to a permitted explosive containing potassium chlorate mixed with mononitronaphthalene, dinitrotoluene, and a little castor oil. Another variety of cheddite contains ammonium perchlorate.

One of the most powerful explosives known is tetranitro-aniline, and a similar compound tetranitromethyl-aniline, known as "tetryl," is already used for detonators in place of mercuric fulminate. Another compound which has recently found application as a detonator is lead hydrazoate or azide, PbN_6 , derived from hydrazoic acid or azoimide HN_3 . The acid itself when in the pure anhydrous state and some of its organic

derivatives are among the most dangerously explosible compounds known, as they sometimes explode violently without obvious cause. But several of the metallic salts, such as the lead salt mentioned above, and the barium salt, are fairly stable and can be manipulated without risk, if proper precautions are taken.

A new explosive, which is said to exceed in power all others and has a remarkable rate of detonation, is known as "cyclonite" or "hexogen"; it is made by the action of nitric acid on hexamethylene tetramine, the product of the reaction between formaldehyde and ammonia (p. 338). The substance has the chemical name of cyclo-trimethylene-trinitramine, and it has been suggested for use as an initiating explosive.

In blasting operations gunpowder and detonators are fired by a time fuse or electrically. The time fuse is a case containing gunpowder which is made to burn at a known rate, generally 2 feet per minute. The instantaneous fuse which burns at the rate of 100 to 300 feet per second affords the means of firing many charges simultaneously.

Enough has now been written to show the reader the general character of the chemical mixtures and compounds employed for military and naval use and for the peaceful purposes of the miner. But the subject is a very extensive one, and those who desire more technical information can best be advised to read the article on Explosives in Thorpe's *Dictionary of Applied Chemistry*.

An interesting application of explosives to the purposes of agriculture has attracted some attention during recent years, especially on the other side of the Atlantic. In new countries land has often to be cleared of wood and sometimes of masses of rock before it can be brought into cultivation. In order to get rid of trees it has been the custom in past times to burn them and leave the stumps to rot, before attempting their removal. This necessarily occupies a good many years, and the work is difficult and laborious.

As soon as modern explosives became available the idea of blowing up such obstructions naturally arose and has been put into operation on a considerable scale. But latterly the use of dynamite has been resorted to for the purpose of preparing holes for planting fruit trees and for loosening the soil between trees in orchards. As with every newly introduced practice there has been evidence of some degree of exaggeration in the reports

which have appeared in the press concerning the advantages of soil explosions.

The phenomena of combustion and explosion in gases have an interest both for the scientific man and for the coal miner, exposed as he is in the majority of pits to imminent risk in his daily work.

During the last sixty years great advances have been made in the theory of gaseous explosion, and in the knowledge of the rate of transmission of an explosion wave. The first steps in this direction were taken by the famous French chemist, M. Berthelot. At the time of the siege of Paris in 1870, Berthelot, then Professor in the Collège de France, became President of the Scientific Committee of National Defence. The superintendence of the manufacture of explosives to be used against the enemy naturally led him, after the war, to turn his attention to the systematic investigation of the phenomena of explosions. In the result he was able to connect the maximum velocity of the flame in a mixture of gases with the mean velocity of the molecules, according to the kinetic theory of gases. A long series of researches on the propagation of flame through mixtures of gases and on cognate subjects was begun by Messieurs Mallard and Le Chatelier in 1879, and the work of these distinguished French investigators is still frequently referred to. Work on this subject is still being carried on in England and in other countries, because of its importance in connection with the avoidance of explosions in coal mines.

A very important discovery was made in 1880 by the late Mr. Harold B. Dixon, then Professor of Chemistry in the University of Manchester. Dixon found that carbon monoxide mixed with oxygen, when dried as perfectly as possible, by long contact with phosphoric oxide, does not explode when an electric spark is passed through the gas. The admission of a minute trace of water vapour at once restores to the mixture its inflammability. Similar observations were made by the late Professor H. Brereton Baker, until recently Director of the Department of Chemistry in the Imperial College of Science and Technology, South Kensington. Dr. Baker's experiments showed that carbon, sulphur, and even phosphorus, when carefully dried, refuse to burn in oxygen when heated above the temperature at which they usually ignite. He also found that ammonia mixed with hydrogen chloride, and nitric oxide with oxygen are

indifferent when the gases are well dried. These results have been the subject of much speculation, but it is still not known definitely why quite small traces of water vapour are able to bring about reactions which do not take place in the perfectly dry gases.

Notwithstanding the greatly increased knowledge in our time about the properties of inflammable gases and of the conditions prevailing in coal pits, it is, unhappily, true that disastrous explosions continue to occur, in which many lives are lost, as they were before the invention of the safety lamp, in 1817, by Sir Humphry Davy. This fact is, of course, no ground for argument against the utility of the safety lamp.

The explosions which occur are due either to abuse of the lamp, to gross neglect of rules by miners, to blown-out shots, or some other cause. Among the sources of danger not recognised a few years ago is the accumulation of fine coal-dust in many workings.

Attention was first called to the subject by Mr. William Galloway so long ago as 1876, and much discussion and experimentation has been carried on since that time. The presence of fine coal-dust suspended in the air of a mine has long been known to add to the danger of explosions when they occur from presence of fire-damp; but it has only been recognised within recent years that dust alone, diffused through air, forms an explosive mixture through which flame is propagated, when once started, with the violence characteristic of gas explosion.

The English experiments, which form part of a comprehensive scheme for the investigation of the factors liable to cause explosions in coal mines, were at one time carried out at Altofts in Cumberland, but the work has now been transferred to the new Safety in Mines Research Board Experimental Station near Buxton, Derbyshire. The observations on dust explosions are generally carried out in a long iron gallery, made by bolting together a number of cylindrical iron boilers. In this gallery it is possible to cause dust explosions extending over several hundred feet, and the propagation of the flame and the pressure variations can be studied by means of instruments inserted at regular intervals. The work carried out under the direction of Professor R. V. Wheeler, Professor of Fuel Technology in the University of Sheffield, has shown definitely that dust explosions do not depend on the production of gas from the dust by a preliminary process

of distillation ; an explosion can even be propagated through a cloud of charcoal in air.

The fact thus established is consistent with what is known of other dust explosions, as in flour mills, where there can be no question of the existence of inflammable gas in the atmosphere.

It has been found that by the admixture of sufficient stone dust to finely powdered coal the danger of inflammability is greatly diminished, and the Mining Acts of Great Britain make stone-dusting compulsory in order to diminish the danger of coal dust explosions. There is no doubt that this development, resulting from purely scientific studies, has resulted in the saving of many lives.

With the object of limiting the risk of explosions in coal mines, whether originating from gas or dust, the explosives to be used in fiery or dusty mines have to pass a Government test. A testing gallery has been erected at the Buxton research station, and there the effects of various explosives on an explosive mixture of gas, coal dust, and air are carried out. No explosive is passed for use in coal mines until it answers certain tests which indicate that it is reasonably safe.

Strictly speaking, there is no such thing as a perfectly safe explosive ; under certain unfavourable conditions they will all ignite gas or coal-dust, but the "permitted test" does enable the various explosives to be sorted into grades of safety, and only those which have shown themselves to be the safest are allowed to be used.

The "safety" or "permitted" explosives in common use in British coal mines consist of an explosive substance, generally nitroglycerine or T.N.T., mixed with a relatively large proportion of an inert salt, such as common salt (sodium chloride), borax or ammonium oxalate. The object of the salt is to act as a cooling material, thus preventing the temperature of the explosion flame reaching that at which the coal dust-air and methane-air mixtures are likely to explode. Mixtures of 80 to 90 per cent of ammonium nitrate, together with T.N.T. or nitroglycerine are also used for the same purpose.

A new development in connection with safety explosives is the use of the so-called Cardox cartridges, which contain liquid carbon dioxide under pressure. They are set off by passing an electric current through a mixture of two substances, such as a phenolic product and potassium chlorate, which generate a large

amount of heat when they combine chemically. This heat causes the liquid carbon dioxide to evaporate rapidly, and the volume of gas is so large that the process takes place with explosive violence. Since no flame is produced during the explosion there is no danger of setting off the explosive mixtures present in the atmosphere of a coal mine.

CHAPTER XXVII

FIXATION OF ATMOSPHERIC NITROGEN

At the meeting of the British Association for the Advancement of Science held at Bristol in 1898, Sir William Crookes in his address as president drew attention to what he called the "Wheat Problem." In the course of his discussion of the facts he produced something approaching a serious sensation by the statement that "England and all civilised nations stand in deadly peril of not having enough to eat. As mouths multiply, food resources dwindle. Land is a limited quantity, and the land that will grow wheat is absolutely dependent on difficult and capricious natural phenomena."

It is true that he added to this alarming view, "I hope to point a way out of the colossal dilemma. It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty."

Fortunately for public peace of mind some relief from anxiety was provided a few months later in a letter addressed to *The Times* on December 2nd, 1898, by Sir John Bennett Lawes and Sir J. Henry Gilbert, the famous experimental agriculturists of Rothamsted, England. They said: "To sum up the world's wheat supply it may be said that whilst wheat is capable of producing very large crops under favourable conditions as to soil, climate, and manuring, it possesses a remarkable power of obtaining food from a poor soil. It can stand a considerable amount of frost, and it can thrive over an immense area of the world's surface. Although endorsing all that Sir William Crookes says as to the importance of wheat as a food, we cannot adopt his desponding views in regard to the future supplies of it.

Wheat breeders have also succeeded in raising varieties more suitable to local conditions than the older sorts, and therefore in improving yields, while better rotations and more manure are now used than formerly.

Crookes' remedy for shortness of wheat supply was the production and application to the land of much larger amounts of nitrogen in the form of nitrate. In reviewing the world's annual wheat crop, and the known results of applying nitrate of soda to the experimental plots at Rothamsted, he calculated that to raise the 12.7 bushels per acre, which was the average yield of wheat of the world's crop, to 20 bushels, it would require 12 million tons of nitrate annually to be distributed in varying amounts over the wheat-growing countries of the world, in addition to the $1\frac{1}{4}$ million tons already absorbed by various crops. But though Lawes and Gilbert would regard a cheap and liberal supply of nitrate as a very great boon to the agricultural world, they thought it very doubtful whether an average of 20 bushels per acre would be obtained year after year the world over by the annual application of 12 million tons of nitrate. They pointed out that if nitrate were used alone the available minerals such as potash and phosphate would soon show a deficiency.

There can be no doubt as to the benefit derived from the use of nitrogenous manures, but there can also be no doubt that at one time there was a danger of the supplies of natural nitrate becoming exhausted before the end of the present century. This substance occurs in the rainless district in the northern

provinces of Chile between the Andes and the coast. In 1898, when Sir William Crookes delivered his famous address, the export of Chile saltpetre, as the sodium nitrate is called, was 1,200,000 tons per annum, but the amounts rose steadily and had attained more than double this quantity before serious competition from other forms of nitrogen compounds resulted in a marked reduction.

Before considering the available sources of combined nitrogen made by chemical methods, another natural form of nitrogenous material, namely, animal manures, must be mentioned. In the form of the dung of animals, fed on pasture, a certain amount of the nitrogen derived from the grasses and other herbage is transferred to the arable, including wheat, lands. It is impossible in this connection to avoid deploring the sewage system which is so generally prevalent in towns and cities, for by this means practically the whole of the nitrogen from the food of the human population is irrecoverably wasted. A simple calculation will show how very great is the waste. Assuming that in round numbers there are 30 million adults and 15 million children in the United Kingdom, and that each adult excretes 1 ounce of urea and a child $\frac{1}{2}$ ounce of urea in a day, these figures correspond to 381,790 tons of urea in the year. This quantity of urea contains the same amount of nitrogen as 839,942 tons of ammonium sulphate or 1,081,744 tons of sodium nitrate. A small quantity of this nitrogen passes direct to the soil and a small quantity to sewage farms, but the saving is practically insignificant. The rest, with the phosphates, is discharged into the sea.

In all pasture land a certain amount of fixation of atmospheric nitrogen is always going on through the agency of bacteria. And it is fortunate that this is so, for without the secret, obscure operations of such tiny things as the *azotobacter*, *clostridium*, and a few other organisms, the necessary stimulant would be missing from large parts of the earth's surface. The albuminous matters thus stored up in the clovers and other leguminous plants yield up their nitrogen again by decay, ammonia passing into the soil and becoming the food of another generation. Here it may perhaps be as well to warn the reader against confusing the action of the bacteria which bring atmospheric nitrogen into chemical combination producing protein substances in the plant, with the action of those other properly called nitrifying organisms

That we may have considerable fluctuations in produce and in price, the result of war, or of the vicissitudes of the seasons in different countries, is very probable ; but we believe that there will always be a sufficient supply forthcoming for those who will find the money to purchase it at a remunerative price."

To this assurance from so respectable an authority may be added a few considerations arising out of the progress which has been made by agriculture in the years which have elapsed since their words were written. The production of wheat for the whole world has increased very largely for several reasons.

Wheat is now grown over large areas not counted on in 1898, including Australia, India, Egypt, South America, while it has increased enormously in Canada and considerably in Russia and the United States.

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by which ammonia is converted first by one microbe into nitrite, and then by another into nitrate. These operations are of great physiological importance as bringing the nitrogen into an assimilable condition, but they add nothing to the soil. The farmer then must look for cheap nitrogen in the form of ammonium sulphate or a nitrate to the chemist, in accordance with the indication of Sir William Crookes in 1898.

Mention has been made in an earlier chapter of the recovery of ammonia, as ammonium sulphate, from the distillation products of coal, but this source of chemical nitrogen has now become relatively of minor significance because of the enormous development in the fixation of atmospheric nitrogen in the form of compounds suitable for addition to the soil.

Up to comparatively recent times gaseous nitrogen was described in chemical text-books as a very sluggish substance, and was often stated, quite improperly, to be incapable of entering into chemical combination with other elements by any direct method. It constitutes four-fifths of atmospheric air, and is usually said to serve the purpose of diluting the oxygen of the air, which would otherwise be too stimulant for the health of the animals which live in it. There is a certain fallacy implied in this statement. If an atmosphere of pure oxygen had been provided as the outcome of the chemical changes which attended the early history of the planet there can be no doubt that the animal organism would have adapted itself to it. It is pretty certain that the composition of the earth's atmosphere has changed considerably since life appeared on the globe, and the physiological processes going on in the present animal and vegetable inhabitants of the earth are the result of adaptation. It is true that atmospheric nitrogen appears to take no direct part in the animal economy. But it is now known that certain plants by a mechanism of their own, namely, the nodules swarming with bacteria which are formed on the rootlets of plants of the natural order *Leguminosæ*, the bean and pea tribe, have the power of taking in the nitrogen of the air and using it in building up some of the albuminous or protein compounds contained in their tissues. Often, however, plants derive their nitrogen from chemical compounds which are formed in minute quantity in the atmosphere.

Of these probably the ammonia results from products of decay of animal and vegetable remains escaping into the air. But the

oxides of nitrogen which are formed, and which come down to the soil in the form of nitrous or nitric acid with the rain, are undoubtedly produced by electric discharges taking place through the atmosphere, perhaps more or less at all times, but especially during thunderstorms. This production of nitrate by electricity cannot only be demonstrated in a few minutes on the lecture table, but has become the basis of a most important manufacture.

It is evident that the gas nitrogen is not so inert as was at one time believed, and in fact there are at present in operation on a large scale at least three important processes in which different chemical reactions are utilised to fix atmospheric nitrogen. To such an extent has this industry developed since 1919 that at the present time the world's capacity for the production of fixed nitrogen compounds is considerably in excess of the demand. This position can, however, only be regarded as temporary, because there is a great deal of room for expansion in the utilisation of nitrogenous substances for agricultural purposes. The following figures, taken from an evening discourse given by Dr. R. E. Slade at the British Association meeting on September 9th, 1930, show the quantity of fertilisers containing nitrogen used in the more important consuming countries of the world in 1928; the figures are expressed in terms of nitrogen, and the variation of the amounts utilised per acre in different countries is very significant.

CONSUMPTION OF FERTILISERS, EXPRESSED AS
NITROGEN, IN 1928

Country.	Tons.	Pounds per acre of arable land.
Germany	516,200	.. 22.3
United States	383,600	.. 2.4
France	166,900	.. 6.7
Japan	113,300	.. 16.8
Holland	73,400	.. 70.6
Italy	68,300	.. 4.7
Spain	67,300	.. 3.8
Belgium	63,600	.. 45.9
Great Britain	61,600	.. 10.4
Poland	54,600	.. 2.7
Total world production	1,843,200	..

Although a variety of different methods has been suggested from time to time for the production on the large scale of compounds suitable for use as fertilisers from the nitrogen of the air, three only of these are responsible for most of the fixed nitrogen produced to-day. These processes, in the historical order of their industrial development, and the order in which they will be described, are :

1. The Arc Process, leading to the production of nitric oxide, and thence to nitric acid and nitrates.
2. The Cyanamide Process.
3. The Haber Process, in which ammonia is the product.

The first two depend essentially on cheap electricity, particularly the arc process which uses five times as much power as that employed for the fixation of an equivalent amount of nitrogen as cyanamide. It is true that the only raw material is air, nevertheless the arc process, which was recently reported to be responsible for only one-twentieth of the total nitrogen fixed in the world each year, is gradually becoming obsolete. The Haber process can be independent of electric power, provided cheap fuel, generally coke, is available, although it can be operated economically where coke is expensive provided electricity is cheap. For this and other reasons, the application of the Haber principle, in one of its several possible forms, is extending all over the world, and it is estimated that about three-quarters of the atmospheric nitrogen is now being fixed by this method.

The Arc Process

So long ago as 1781 and the few following years experiments placed on record by the Hon. Henry Cavendish show that he had established the fundamental facts which more than one hundred and twenty years later have found practical application on a large scale. He found that when hydrogen and air are exploded together the water which is formed is always accompanied with a small quantity of nitric or nitrous acid. He also showed that when common air mixed with some oxygen is exposed to electric sparks the mixture is wholly absorbed by an alkaline solution with production of common nitre. (See passage quoted in connection with discovery of Argon, p. 125.)

Attempts to utilise these facts for manufacturing purposes led to no practical result till in 1897 Lord Rayleigh gave an account



FIG. 124.—POWER HOUSE AT SVAELGFOS, SUPPLYING NOTODDEN FURNACES



FIG. 125.—ARC-FURNACES AT NOTODDEN

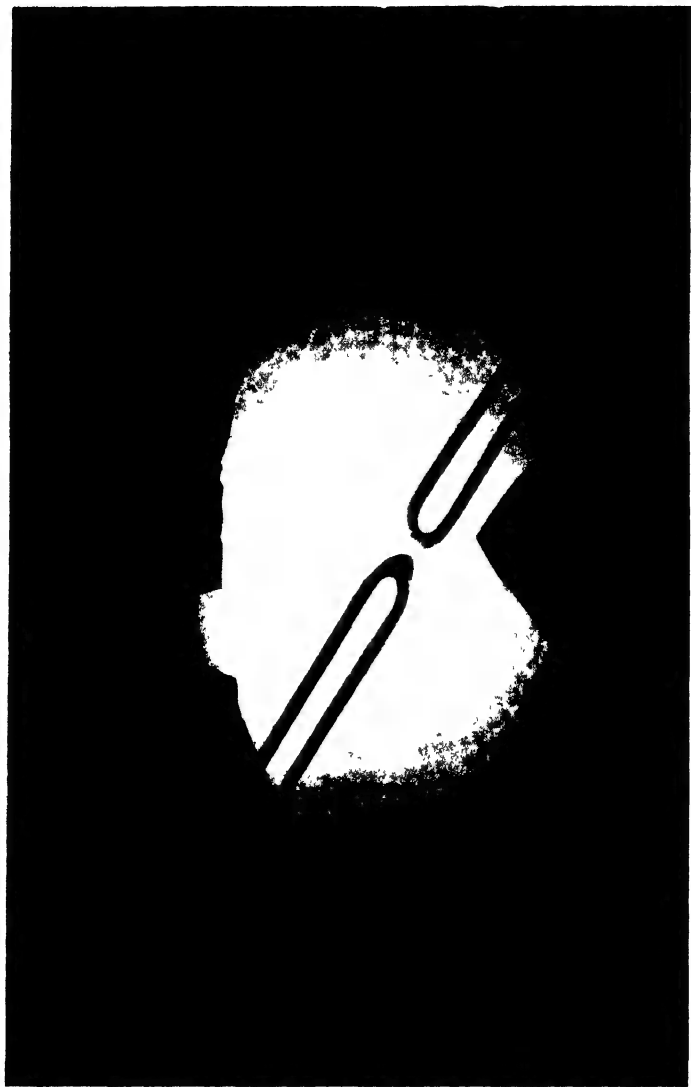
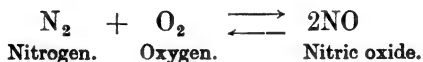


FIG. 126.—BIRKELAND AND EYDE ARC FLAME

of his "Observations on the Oxidation of Nitrogen Gas" in the Transactions of the Chemical Society. The experiments described were made in connection with the isolation of argon from air by removal of the nitrogen, and there can be no doubt that their publication gave encouragement to the idea that it would be possible to utilise the process for the production of nitric acid and nitrates. Passing over the work of the numerous experimenters attracted to the subject in all the civilised countries of the world, it may be noted as an interesting fact that the first practical application of the principle of electric combination of atmospheric gases to the production of nitrates was made by two Englishmen, McDougall and Howles, in 1899. Their works were not commercially successful, and another attempt was made by Bradley and Lovejoy in 1902 in connection with the use of water from Niagara, but it lasted only two years.

The first practical success was achieved by Dr. Samuel Eyde, engineer of Christiania, in association with Professor Kristian Birkeland,¹ who established works at Notodden in Norway. Their process consists in passing air through a flaming electric arc, in which at a temperature of over 3000° C. the oxygen and nitrogen combine to a small extent (about 5 per cent) to form a compound, nitric oxide, thus :

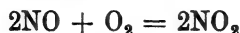


The flaming arc is produced by passing an electric arc, by means of alternating current, between two electrodes made of thick copper tubing through which a stream of water passes for cooling purposes. The electrodes are placed between the poles of a powerful electro-magnet which has the effect of causing the arc to spread out into a circular sheet of flame (Fig. 126) about 7 or 8 feet in diameter. Two other forms of arc, namely, the Schönherr and the Pauling, have been employed, but they do not appear to have displaced the original Birkeland-Eyde process.

It will be noted in the equation given above for the reaction taking place in the arc that double arrows are used ; this means that not only do oxygen and nitrogen combine to form nitric oxide, but the latter tends to split up again into its constituents. In order to avoid this possibility the gases containing a little nitric oxide are forced rapidly past the arc, so that their

¹ Professor of Physics in the University of Christiania, Norway.

temperature immediately falls to 800° or 1000° C., and they are cooled further by being conducted to boilers where the heat is utilised to raise steam, and then finally cooled by passage through pipes surrounded by cold water. The gases then pass into vertical iron cylinders, lined with acid-proof stone, where the nitric oxide combines with oxygen present from the air forming nitrogen dioxide (or peroxide), thus :



Nitric oxide. Oxygen. Nitrogen dioxide.

The gases are now driven into absorption towers where the nitrogen dioxide is dissolved out by means of water, and nitric acid is formed. These towers are tall stone structures, of which the height, approximately 65 feet, may be judged by the figures of two men visible in the adjoining illustration. They are filled with broken quartz over which water is continually trickling. The gases enter at the base of the first tower, and by means of a large earthenware pipe pass to the top of the second, through which they pass downwards to the bottom of the third tower. They then pass through two wooden towers in which they are washed by a solution of carbonate of soda. The liquid collected in the first series is pumped backward, the product of the third into the second and from the second into the first, and thus the nitric acid formed is concentrated, so that the first tower yields an acid containing 50 per cent of nitric acid. The soda towers yield nitrite of soda.

To carry the gases forward each row of towers is provided with centrifugal fans made of aluminium which is not attacked by nitric acid.

The nitric acid collected from the towers is stored in granite tanks, neutralised by calcium carbonate, and after the addition of a small quantity of lime the solution is evaporated¹ and the residue, after solidification and granulation in a mill, is run into iron drums, in which it passes into commerce under the name of "Norwegian Saltpetre" or "Air Saltpetre." Some of the nitric acid is also concentrated, without neutralisation, and sold in this form.

The phenomenal growth of the arc process for the fixation of

¹ All the necessary evaporations are effected by the waste heat of the electric furnaces, without the consumption of coal. This is a very important consideration from the industrial point of view.

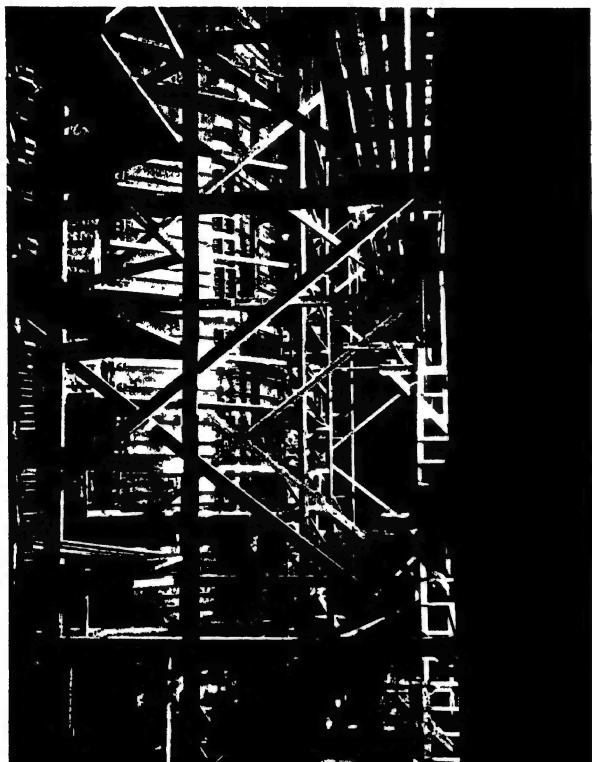


FIG. 127 — ABSORPTION TOWERS FOR OXIDES OF
NITROGEN, AT NOTODDEN

nitrogen in Norway is shown by the following figures for the approximate rate of electrical power usage since 1903.

ELECTRIC POWER USED FOR ARC PROCESS IN NORWAY

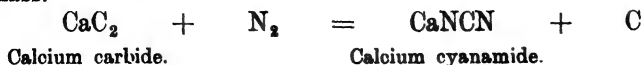
Year.	H.P.
1903	25
1905	2,500
1907	42,500
1911	200,000
1925	380,000

Owing to the competition by the other methods of fixing nitrogen, now to be described, the rate of increase has not been maintained, and the output from the arc process appears to have reached a limit ; it has, in fact, been stated that the large works at Rjukan are being converted for operating the Haber process (*vide infra*).

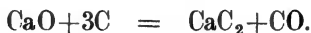
The Cyanamide Process

The cyanamide method for the fixation of nitrogen was invented by Frank and Caro towards the end of the nineteenth century, whilst trying to find a new method for making cyanide for use in extracting gold from its ores. It was first worked on a commercial scale in Italy in 1905, and three years later production was started at Odda in Norway, where in the four years from 1908 to 1912 an average of 20,000 h.p. of electricity was used for this purpose, rising to nearly 50,000 h.p. in 1912. In the meantime a plant had been erected in Canada, where electricity made from the water-power of the Niagara falls was utilised ; this is now one of the world's largest cyanamide plants, having an output capacity of nearly 250,000 tons per annum. Large plants were also erected in the United States of America, at Muscle Shoals, Alabama, during the war, and a very considerable amount of cyanamide is also made in Germany. Owing to the cost of electricity this process is not worked in England.

The production of calcium cyanamide depends on the combination of calcium carbide with nitrogen gas under the influence of a moderately high temperature, produced by an electric current passing through carbon resistances embedded in the mass.



The first stage in the series of operations is the production of calcium carbide. The materials employed for this are lime, made by heating limestone and carbon in the form of anthracite. When these, mixed together in proper proportions, are heated in electric furnaces to a temperature approaching 3000° C. (5432° F.), a reaction ensues in which the carbon unites with the oxygen of the lime forming carbon monoxide gas, and with the calcium, forming calcium carbide as the chief constituent of the solid residue :

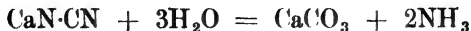


Lime. Carbon.

The separation of the requisite nitrogen from the atmosphere by the Linde liquefaction process has already been described (see Nitrogen, p. 248), and we may, therefore, now proceed to examine the operations involved in the production of cyanamide. The first step is to reduce the carbide to powder, and to avoid access of moisture the grinding is performed in air-tight apparatus. The powder exposed to contact with nitrogen at a temperature of 800° to 900° C. absorbs the gas, and the process is attended by the evolution of much heat. The heat liberated is, however, not sufficient to make the process automatically continuous, and so further heat is supplied by means of an electric current which is passed through a carbon rod placed in the centre of each drum-shaped furnace (Fig. 128). The final product is known as "nitrolime"; it contains nearly two-thirds of its weight of calcium cyanamide, $\text{CaN}\cdot\text{CN}$, corresponding to a total content of nitrogen equal to 20 to 22 per cent.

Nitrolime also contains about 20 per cent of free lime, 7 to 8 per cent of silica, alumina, and iron as impurities, and 14 per cent of carbon, which is in the form of graphite.

By the slow action of atmospheric air, which contains carbon dioxide and moisture, cyanamide is converted into urea, and hence old specimens of nitrolime may contain appreciable quantities of this substance. Its use as a manure is dependent on the fact that in the soil, in contact with moisture, the whole of the nitrogen, whether present as cyanamide or as urea, is slowly converted into ammonia :



Calcium cyanamide.

Ammonia.

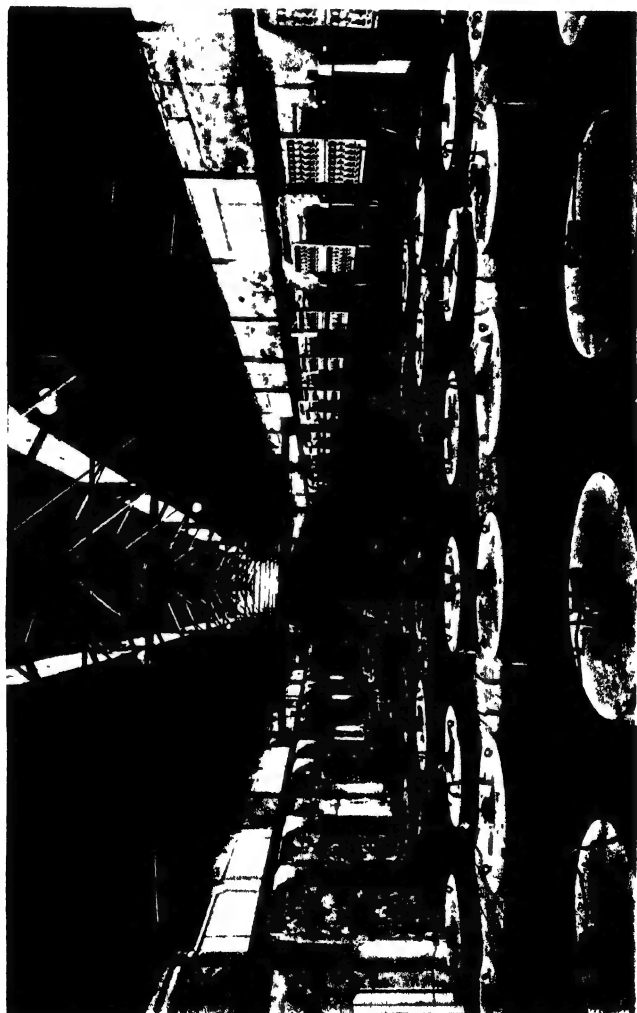


FIG 128.—CYANAMIDE FURNACES, ODDA, NORWAY



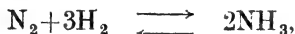
FIG. 129 —SYNTHETIC AMMONIA FACTORY, BILLINGHAM, DURHAM

(By courtesy of the Imperial Chemical Industries, Ltd.)

This process may be expedited by heating the nitrolime with super-heated steam and a little soda ; the ammonia evolved is collected, neutralised with an acid and sold in the form of an ammonium salt, generally sulphate or nitrate.

The Haber Process

The production of ammonia by the combination of hydrogen and nitrogen gases represents one of the most striking achievements of chemical industry, for by this means nearly a million tons of nitrogen are being fixed annually, yet in 1905, when the late Professor F. Haber,¹ then of Karlsruhe, Germany, commenced his experiments quite eminent chemists stated that nitrogen and hydrogen could not be made to combine under the influence of heat. In spite of this view Haber continued his studies of the equilibrium, under various conditions, between nitrogen (N₂), hydrogen (H₂), and ammonia (NH₃) gases represented by the equation



and he showed that ammonia could be obtained to some extent by the union of nitrogen and hydrogen ; the higher the pressure and the lower the temperature the greater was the proportion of these gases converted into ammonia. Since the interaction of nitrogen and hydrogen becomes very slow as the temperature is lowered, Haber found it advisable to use a catalyst (see chapter XII) in order to speed up the process, and he showed that, on a small scale at least, it was feasible to obtain quite good yields of ammonia by this method.

¹ Fritz Haber was born at Breslau on December 9th, 1861, and studied at Berlin, Heidelberg, Charlottenburg and Zurich. In 1894 he became an assistant at the Technical High School in Karlsruhe, and two years later was appointed Professor of Industrial Chemistry there ; this post he retained until called to the Directorship of the Kaiser-Wilhelm Institute of Physical Chemistry and Electrochemistry at Dahlem, Berlin. Haber's most important work was in connection with the thermodynamics of gas reactions, as a result of which the process for the fixation of nitrogen, bearing his name, was invented ; he also carried out important researches in electrochemistry. During the war he assisted in the development of methods for obtaining the much needed nitrates from atmospheric nitrogen, and is also said to have been responsible for the use of the deadly " mustard gas." In 1933 Haber left Germany for political reasons, and migrated to England, continuing his work at Cambridge. He died on January 29th, 1934, on his way to the South of France, where he had gone to try to recover his failing health.

In 1910 the great German chemical firm, the Badische Anilin und Soda Fabrik, now part of the Interessen Gemeinschaft Farbenindustrie A.-G., began to take an active interest in the problem of fixing atmospheric nitrogen, and after three years' work under the direction of Dr. C. Bosch, the practical difficulties involved in working at high pressures on a large scale, and other problems connected with the process, were overcome to such an extent that a plant for the manufacture of ammonia was erected at Oppau, near Ludwigshafen-am-Rhein, in 1913. The Haber-Bosch process, as it is generally called, involved working at pressures of about 200 atmospheres (3000 lbs. per square inch) and a temperature of approximately 500° C., with iron in a spongy form as the basis of the catalyst.

Shortly after the completion of the Oppau factory war broke out and Germany was unable to obtain the nitrates from Chile which were essential for the manufacture of explosives, and so every effort was concentrated on the production of ammonia, since the latter could be converted into nitric acid, and hence into nitrates, by the well-known process worked out by Ostwald (see p. 212). A second factory for making ammonia by the Haber-Bosch process was, therefore, erected at Merseburg in Saxony, and by the end of the war it is believed that the two plants were producing ammonia and nitrates at the rate of 300,000 tons of nitrogen per annum. The present capacity of the German factories for the fixation of nitrogen as ammonia is estimated to be as high as 850,000 tons.

Although Britain and the United States were not so hard pressed in the matter of nitrate supply during the war, the large amounts of this substance being used up stimulated both countries to attempt the fixation of nitrogen from the air by the Haber-Bosch method; in America a factory was erected at Sheffield, Alabama, but owing to faulty design it was finally closed down early in 1919, after being in operation only for three months. It is perhaps owing to this unfortunate experience that the United States chemical manufacturers have not shown the enthusiasm for the Haber process commensurate with the extent to which other chemical industries have been developed; nevertheless it was estimated recently that factories in the United States have a capacity for fixing 168,000 tons of nitrogen per annum as ammonia.

The history of the nitrogen fixation industry in England is

best told in the words of Colonel G. P. Pollitt,¹ who played an important part in its development.

"The difficulties of obtaining supplies of Chile nitrate proportionate to the enormous demands made by the fighting forces became almost insuperable, and the Government decided in 1917 to erect a plant on the Haber-Bosch principle.

"Owing to the very heavy calls upon the Government's scientific staff during this period, however, very little progress was made, and, when the end of the war came, the Government had to decide whether they should endeavour to carry on this industry themselves, or whether they would be content by encouraging private enterprise to take it up where they had left off.

"At this stage, at the request of the Government, the matter was taken over by Messrs. Brunner, Mond, through their subsidiary, Synthetic Ammonia and Nitrates, Ltd.—now part of Imperial Chemical Industries Ltd. This latter company appointed a staff of scientists and others, and attacked the problem from the beginning. They were unable to obtain the information they required as to working the process, from Germany or elsewhere, and were compelled to work the process out for themselves. The steps taken by them were as follows :

"After preliminary study of the problem, they took over a tract of some 800 acres at Billingham, near Stockton-on-Tees. They erected thereon a laboratory specially designed for the type of work they were endeavouring to do, and differing entirely from any other laboratory in the kingdom, inasmuch as it had to undertake a new technique, namely, that of high-pressure work.

"In this laboratory was erected a complete model of a synthetic-ammonia plant, beginning with water-gas and ending with ammonium sulphate ; this whole plant was capable of being worked continuously, and upon a 1/300 scale, based on the plant it was proposed to erect first upon the Billingham site.

"While this work was going on, a plant to make two tons of ammonia a day was simultaneously erected at the works of Messrs. Castner-Kellner, Ltd., where considerable quantities of hydrogen, made as a by-product in the caustic soda and chlorine industry, were available. This experimental plant, since greatly increased, came into operation in May, 1921. . . .

¹ Medal Address : *Journal of the Society of Chemical Industry*, 1927, p. 291 T.

"The next step was to erect a complete plant at Billingham for the manufacture of 120 tons of sulphate per day, which was subsequently increased to 250 tons of sulphate per day. This plant came into operation in December, 1923. . . .

"One of our greatest difficulties in establishing the high-pressure industry in this country was due to the fact that it was impossible to obtain . . . the type of valve, joints, etc., required for very high pressures. One of the biggest achievements of our engineers was the development of our own manufacture of this type of apparatus. So satisfactorily was this done that our high-pressure apparatus is in many respects simpler to operate and easier to maintain than low-pressure plant."

The Billingham plant has been extended from time to time and is now believed to have a capacity of about 170,000 tons of fixed nitrogen, in the form of ammonia, ammonium sulphate, nitrates, etc., per annum.

The processes in use in England and in Germany are substantially the same: the hydrogen is obtained from water gas (chapter XIV), and nitrogen by removing the oxygen from air by means of hot coke. Steam and air are passed either together or separately over heated coke, when a mixture of carbon monoxide and hydrogen (from the steam) and nitrogen (from the air) is obtained. More steam is passed in and the mixture forced over a catalyst consisting of ferric oxide in order to convert the carbon monoxide into dioxide, as already explained (p. 243), an additional amount of hydrogen being produced at the same time. The gases are compressed to about 25 atmospheres and the carbon dioxide dissolved out by means of water; the last traces of carbon monoxide, about 1 per cent, are removed by passage through a tower containing an ammoniacal solution of a copper (cuprous) salt. If the conditions have been properly regulated the final gas now contains three parts of hydrogen to one part of nitrogen, by volume, these being the correct proportions for the production of ammonia.

The gases are next compressed to about 200–250 atmospheres, and passed into the reaction chambers containing the catalyst. The latter consists essentially of finely divided iron, often made by the reduction of iron oxide, together with small quantities of other substances acting as "promoters." The temperature of the reaction vessels is kept at 500° C.; no extra heat has to be supplied since quite enough is evolved in the chemical reaction



FIG 130 —THE WATER-GAS PLANT, BILLINGHAM

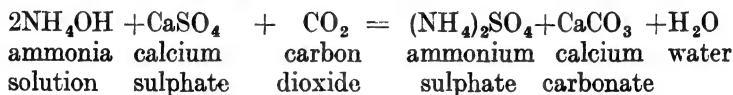
(By courtesy of the Imperial Chemical Industries, Ltd)



FIG 131 —PORTION OF HYDROGEN PLANT, BILLINGHAM
(By courtesy of the Imperial Chemical Industries, Ltd)

between hydrogen and nitrogen to maintain the required temperature. Any fluctuations are adjusted by altering the rate of flow of the gases. About one-tenth of the mixed gases is converted into ammonia; this is removed, generally by being dissolved out in water, and the unchanged nitrogen and hydrogen pass back, with fresh gas, into the catalyst chamber.

The major proportion of the ammonia is converted into ammonium sulphate by means of calcium sulphate, which in the form of the mineral *anhydrite*, is found "in an inexhaustible supply at a depth of 700 feet below the Billingham site." The finely powdered mineral is suspended in the ammonia solution, and then carbon dioxide, obtained from an earlier stage of the process as a by-product, is passed in: a reaction which may be represented by the equation:



takes place. The calcium carbonate is insoluble and is filtered off: the clear solution is then evaporated down until ammonium sulphate crystallises out. The calcium carbonate is either mixed with fertilisers to supply lime to the soil, or used in the manufacture of calcium nitrate.

Some of the ammonia obtained in the process is oxidised to nitric acid, as already explained, and then neutralised and sold in the form of ammonium and calcium nitrates. Ammonium phosphate, ammonium carbonate, and anhydrous ammonia for refrigerating purposes, are also made, and in Germany some of the ammonia is converted into urea which is used not only as a fertiliser but also in the preparation of an important synthetic plastic material (chapter XXV).

Various modifications of the process described here are in use on the continent of Europe, in Japan and probably elsewhere: these involve either differences in the methods for obtaining nitrogen and hydrogen, or in the conditions used for making them combine. The famous French engineer Claude has devised a process for obtaining hydrogen from coke-oven gases, the impurities being mainly removed by liquefying them out at low temperature and under pressure. Where electricity is cheap, but coke fuel expensive, hydrogen is made by electrolysis of water containing a little acid (p. 243); nitrogen can be obtained from

liquid air, as described earlier, or else by burning hydrogen in air so as to remove the oxygen.

In the Claude and Casale modifications of the Haber-Bosch process much higher pressures, in the vicinity of 800 to 1000 atmosphere, i.e. 12,000 to 15,000 pounds per square inch, are employed. It is well known to chemists that the higher the pressure the larger the proportion of nitrogen and hydrogen converted into ammonia, but the difficulties of working at extremely high pressures were so great that in English and German factories a compromise was struck and pressures of about 200 atmospheres were used. With the invention of special steels, capable of withstanding great pressures, and further developments in technique the use of 1000 atmospheres has become possible. The Claude process claims to involve lower cost of installation, greater simplicity of plant, and reduced labour.

Before closing this chapter it will be of interest to give some data concerning the world's nitrogen industries. The chief sources of nitrogenous compounds, consisting mainly of ammonium salts, sodium nitrate and calcium cyanamide, are the by-product ammonia from gas works and coking plants, the naturally occurring nitrate from Chile, and the various forms of synthetic nitrogen. The following figures, expressed in terms of the amount of nitrogen contained in the various products so as to have a common basis for comparison, show the world's production of nitrogenous compounds just before the war and in recent years.

WORLD'S PRODUCTION OF NITROGEN COMPOUNDS

(EXPRESSED AS TONS OF NITROGEN)

Source.	1912-13.	1927-28.	1929-30.	1932-33.	1933-34.
By-product Ammonia	384,000	407,500	475,800	297,300	351,000
Chile Nitrate . .	436,800	219,600	464,000	70,800	85,200
Synthetic products .	95,200	763,800	1,263,700	1,308,800	1,350,500

The increase in the production of synthetic nitrogen compounds is most remarkable, and it is estimated that the *capacity* of the whole world in this respect is as high as 3,300,000 tons of nitrogen. By-product ammonia is barely holding its own, and the production of Chile nitrate has collapsed to such an extent as almost to exterminate the industry. The economic aspects of the problem may be open to discussion, but no one can fail to appreciate the remarkable achievements associated with the chemistry of nitrogen.

PART IV

MODERN PROGRESS IN ORGANIC CHEMISTRY

CHAPTER XXVIII

SUGAR

It is very doubtful whether the sugar cane was known in ancient times, for the word translated *sweet cane* in Isaiah (chap 43, v. 24) and Jeremiah (chap. 6, v. 20) appears to have referred to the sweet-smelling calamus or reed, and the production of sugar as an article of food probably belongs to a much later period. It is mentioned in some Greek and Roman writers as used in medicine. The cultivation of the cane seems to have come from the East, and the extraction of sugar practised in early Christian times then passed into Sicily and later into Spain and Portugal. About the fifteenth century the manufacture was established in the West Indies and in Brazil. Hawkins brought sugar to England from San Domingo in 1563, and about this time English planters were prospering in Barbadoes.

It is a little difficult to realise the conditions under which our remote forefathers before this time arranged a dietary with no direct sweetening agent except honey. It is estimated that at the beginning of the eighteenth century about 4 lbs. of sugar were consumed per head of the population in England each year; this had risen to 18 lbs. by 1820 and to 34 lbs. by 1854, and is now about 90 lbs. on the average for each man, woman, and child. In the United States the consumption is slightly higher at 120 lbs. per head in each year.¹ The sugar which is now consumed in such large quantities is a remarkable example of a practically pure chemical compound which serves as an important food-stuff, and is rapidly assimilated when taken into the stomach.

Common sugar exists in the juices of a great many plants and fruits, but the chief supplies of the world are derived from two sources, viz. the sugar cane, which is a tropical plant, and the

¹ For an interesting account of the world's sugar industry, see the *Twelfth Streetfeild Memorial Lecture*, 1929, delivered by Lewis Eynon; published by the Institute of Chemistry.

sugar beet, which is cultivated only in temperate climates. Small quantities of sugar for local purposes are obtained from several species of palm in India and the East, and pass into commerce under the name "joggery." Another source of sugar is the cane maple (*Acer saccharinum*) which grows in some abundance in the northern states of America and in Lower Canada.

The relative extents to which the two main sources of sugar have been utilised are shown by the following figures.

WORLD PRODUCTION OF SUGAR

Year.	Cane Sugar.	Beet Sugar.
1901-2 .	7,000,000 tons ..	7,000,000 tons
1913-4 .	9,700,000 „ ..	8,800,000 „
1927-8 .	16,700,000 „ ..	8,300,000 „
1932-3 .	16,500,000 „ ..	7,600,000 „
1933-4 .	16,600,000 „ ..	8,700,000 „

The cane sugar is produced mainly in British India (about 5 million tons per annum), Cuba (2 to 3 million tons), Hawaii, Puerto Rico, and Japan (each about 1 million tons), and Java, which was once one of the most important producers, but the amounts have recently been curtailed as a result of international agreement. Sugar beet is grown almost exclusively in Europe, the chief countries concerned being Germany and Russia (each about $1\frac{1}{2}$ million tons), France (over 1 million tons), Czecho-Slovakia ($\frac{1}{2}$ to 1 million tons), and England (just over $\frac{1}{2}$ million tons).

Before 1914 almost the whole of the sugar used in Great Britain, nearly 2 million tons, was imported, as very little sugar beet was grown; one or two attempts had been made to develop the sugar beet industry, but these were unsuccessful. After the war the Government introduced legislation to encourage this industry, at first by lowering the duties on home-grown sugar, and later by giving in addition a subsidy, based on the actual yield of beet, to growers of sugar beet. Under the influence of this subsidy, which amounted to an average of about five millions sterling per annum for the years 1925 to 1935, the extent of sugar beet production increased considerably as the following data show. It appears that the subsidy may be withdrawn shortly: if so, the future trend of the sugar beet industry may be quite different.

BEET SUGAR PRODUCTION IN THE UNITED KINGDOM

Year.	Tons.
1927-8	200,000
1931-2	250,000
1932-3	328,700
1933-4	467,000
1934-5	608,000

The current year's production represents about one-third of the total consumption of sugar, so that almost no beet sugar is now imported from abroad ; most of the imported sugar is derived from the cane, and about one-half originates from the British Empire. The refining of sugar is an important industry in Great Britain, since about one and a quarter million tons of sugar, worth some ten millions sterling, are refined each year.

Sugar is obtained from sugar canes by passing them between rollers whereby the juice is squeezed out. The latter then receives the addition of a very small quantity of lime and is heated to boiling to coagulate albuminous matters. After skimming, the clarified liquid is run into a vacuum pan, where it is boiled down, under reduced pressure, and therefore at a lower temperature, till it becomes concentrated enough to concrete into a crystalline mass on cooling. This mass is drained in perforated casks or centrifugal machines whereby the uncrystallisable treacle is removed. Sugar obtained thus has a more or less brownish colour, owing to changes which have been produced in some of the juice during evaporation. To obtain it in the form of white crystals or lumps the raw sugar is dissolved in water, and the syrup is forced through a tall cylinder containing charcoal, where the colouring matter is retained and a colourless syrup runs through. From the latter by concentration in vacuum pans separate crystals may be produced, or by standing in a frame a solid crystalline block may be formed.

Beet sugar is extracted by washing the roots and then cutting them into thin slices which are systematically exhausted of their soluble matters by immersion in successive portions of hot water, so arranged that the already partially charged liquid is used for treating the fresh roots and thus a strong solution is obtained. This is finally drawn off and heated with a little lime, which neutralises acid and coagulates albumin ; carbon dioxide or sulphur dioxide is then passed through to remove the excess of

lime. The liquid is filtered through charcoal and the clear solution concentrated in vacuum pans. In the operation of extraction it should be understood that the process is essentially based on liquid diffusion in which sugar and the salts present pass as "crystalloids" through the walls of the cells of the beet-tissue, while the gummy and albuminous matters being "colloidal" remain for the most part behind in the pulp. Mere expression of the juice would not, therefore, lead to satisfactory results, as the fluid would in that way be loaded with uncrystallisable matters which would be difficult to remove.

Beet contains about 15 per cent of sugar, which even rises under favourable circumstances to as much as 18 per cent. The average content of sugar in British beet is now 17 per cent, and of this only a very small proportion, about one-thirtieth, remains in the waste pulp.

One of the difficulties in the sugar beet industry has been the necessity of working up the whole supply within three months of the beet harvest. This has been overcome by the invention of various processes for drying the beets, so that they can be kept for some time and the extraction of the sugar can be spread over the whole year.

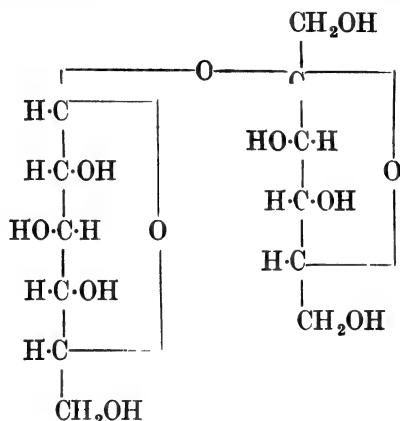
Common sugar belongs to a large class of chemical compounds called "carbohydrates" from the fact that their composition may be expressed by a formula in which there is just the proportion of hydrogen present sufficient to form water with the oxygen. Thus the composition formula of sugar is



in which the number of hydrogen atoms is double that of the oxygen.

Nearly all these substances are important constituents of food, and they may be divided into two main groups, namely, the crystalline sweet substances known as sugars, and the non-crystalline and nearly tasteless constituents of many vegetable tissues such as starch, gum, and cellulose. Both these groups include a great many members or distinct individuals from the chemical point of view, and the interest of the subject has been greatly increased within the last few years by the success which has attended their investigation, so that at present a great deal is known of their constitution and structure. Not only have many of the natural carbohydrates been made by synthetical

laboratory processes, but a large number of purely artificial sugars have been built up which have no existence in nature, or at any rate have not hitherto been discovered. The constitutional formula for common sugar, which harmonises with its properties, is represented as shown below.



This looks rather formidable, but a glance will show that it is essentially made up of two chains each consisting of six atoms of carbon, with which are associated four hydroxyl groups, HO, connected together by the agency of an atom of oxygen which links them.

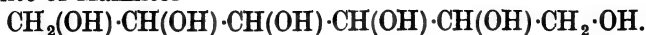
Before proceeding to enquire how this has been determined it may be of interest to examine why sugar possesses a sweet taste and is so soluble in water. This appears to be connected with the presence of the numerous hydroxyl groups attached directly to carbon atoms, which also are linked to one or two atoms of hydrogen. Many compounds having a more or less sweet taste and ready solubility are thus constituted. They are possessed of the chemical characters exhibited by common ethyl-alcohol $\text{CH}_3\cdot\text{CH}_2\text{OH}$, though not its intoxicating properties. Thus :

Ethylene-alcohol or glycol $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$.

Propylene glycol $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$.

Glycerine or glycerol $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$.

Mannite or Mannitol



All these substances have a decided sweet taste, though

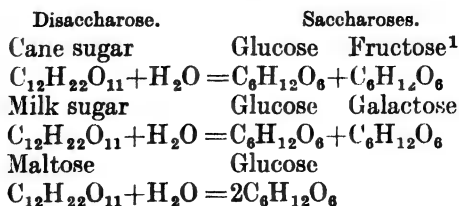
inferior to that of common sugar, and it will be found when the constitution of some of the other sugars is explained that they also contain an abundance of this constituent, hydroxyl, HO. It will be observed, however, that when hydroxyl is associated with carbon which is charged with oxygen instead of hydrogen its function changes and it gives rise to acid.

Thus glycol is sweet in virtue of the hydroxyl and the hydrogen combined with the carbon, but when the two hydrogen atoms are each replaced by one atom of oxygen oxalic acid is the result, HO·CO·CO·OH. The same gathering of oxygen and hydroxyl together, which is usually called carboxyl, is characteristic of hundreds of known acids.

The whole story of the sugars is too technical to be presented in any approach to completeness before the general reader. It will be sufficient if we endeavour to trace the transformations of a few of the more important members of the group, and if possible give some idea of the views entertained by modern chemists as to their constitution.

The origin of cane sugar has been already sufficiently described. Another sugar which has the same composition but very different properties is contained in milk to the extent of nearly 5 per cent. Milk sugar or *lactose* is obtained by evaporating clear whey to a syrup, when on standing the sugar crystallises in hard crusts and crystals which contain $C_{12}H_{22}O_{11}$ united with one molecule of water of crystallisation.

Maltose is another sugar having the same formula which is produced by the action of malt extract, containing *diastase*, on starch, and hence is formed in the preliminary stages of the fermentation of beer or grain spirit. Both these substances are less sweet than common sugar, but all three agree in undergoing a change under the influence of a small quantity of an acid which results in each breaking up into two sugars of a simpler type, the molecule of which contains only six atoms of carbon, and which are called *hexoses* or *saccharoses*.

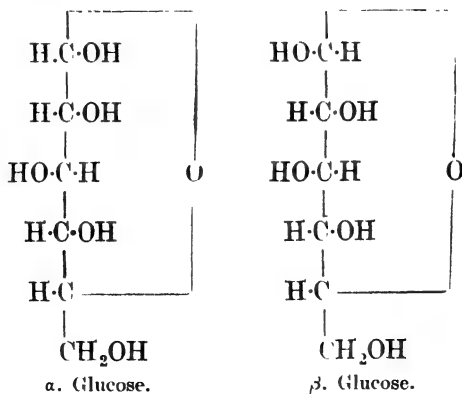


¹ This change occurs when sugar is cooked with sour fruit.

Glucose or grape sugar occurs in ripe grapes and raisins, and is manufactured by heating starch with water till liquefied, and boiling the solution with a small quantity of sulphuric acid. After complete conversion of the starch the liquid is neutralised by adding a slight excess of chalk, filtering, and after passing through charcoal, evaporating the solution to crystallising consistency. Glucose is manufactured for use in preserving fruit and jam, and in the production of beer and so-called "malt" vinegar; it is also used in many forms of sweets and confectionery.

Fructose or fruit sugar is associated with glucose in many fruits. Like glucose it ferments in the presence of yeast and resembles glucose in many properties, differing from it in its action on polarised light. Glucose rotates the polarised ray to the right and is, hence, frequently called dextrose, while fructose rotates to the left and is sometimes called lævulose in reference to this fact.

As a result of recent investigations it is now believed that glucose exists in at least three forms, two of which known as α and β are quite common. They contain the same constituents attached to the six fundamental carbon atoms, but they differ in the arrangement in space of the H and OH groups attached to one of the carbon atoms; this is seen to be the topmost atom in the chains shown below.



The two forms of glucose are readily convertible into one another in solution, the transformation being accompanied by a change in the extent to which the plane of polarised light is rotated.

Amygdalin, described above, is not the only glucoside which yields prussic acid. Researches within recent years have shown that glucosides which, on hydrolysis by their own enzymes, yield this poisonous product are more widely spread than was formerly supposed. Thus the *Lotus arabicus*, a small leguminous plant resembling a vetch, which grows abundantly in the valley of the Nile and is used as fodder, contains a yellow crystalline glucoside together with an enzyme, and when moistened with water and crushed the leaves of the plant evolve prussic acid. Hence the plant is very poisonous to cattle, and the effect is most marked in the young plant up to the period of seeding. Some other plants eaten by cattle contain similar substances and require to be used with caution.

Tannin, which is a very widely diffused vegetable principle which constitutes the astringent agent in many barks, woods, leaves and other parts of plants, is also a glucoside. It yields gallic acid and glucose when hydrolysed. Tannins are not only protective to the plant, but like other glucosides provide a store of reserve material to be used when the plant requires help in the development of buds or leaves or in the ripening of fruit.

Starch and other carbohydrates serve a similar purpose.

It would be unsuitable to these pages to enter into the necessarily long story of the successive steps by which, already long ago, the general character and chemical constitution of the sugars have been unfolded. The history of the researches on the subject dates back to the period, now eighty years ago, when chemical constitution began to be understood, and of course the facts and deductions from them are recounted in all the principal textbooks of organic chemistry. But the steps forward which resulted from Emil Fischer's¹ work thirty years ago

¹ Emil Fischer was born at Euskirchen, near Cologne, on October 9th, 1852; he was at first apprenticed to a timber merchant, but finding the work un congenial he commenced to study chemistry at Bonn, proceeding soon afterwards to Strasbourg where he graduated in 1874. Shortly after graduating Fischer obtained the post of assistant to the Professor of Chemistry in Munich, where he was appointed "Extraordinary" Professor in the analytical department of the University in 1879. Subsequently he held Professorships at Erlangen (1882), Würzburg (1885) and Berlin (1892); at the latter place he was Director of the Chemical Institute of the University, a post he held until his death on July 14th, 1919. Fischer's main researches may be grouped under three heads, each one of which would alone have been sufficient to have made his reputation; they were the study of the sugars, the synthesis of uric acid and related substances (the purines), and the investigation of the proteins and amino-acids. Emil Fischer was elected a Foreign Member of the Royal Society in 1899, and later awarded

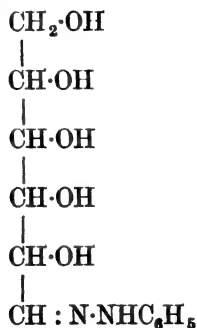


Emil Fischer

represent one of the great triumphs of synthetical chemistry, of which the first stages were indicated in a recent chapter (p. 333), and of which further developments will have to be reported further on.

The first step to be taken in the study of such a class of compounds as the sugars is to discover a method by which the several compounds may be discriminated and recognised even in the presence of one another. Nearly all these compounds are characterised by rotating the plane of polarisation of a ray of polarised light, and this serves as an indication that the molecule contains one or more atoms of carbon in the condition which has been described as asymmetric (p. 201). This alone would be insufficient, but Fischer was successful in finding a chemical reagent, phenyl-hydrazine, with which all the saccharoses unite and with an excess of it interact to produce a characteristic compound, called an osazone, by which each sugar may be separated, purified, and identified.

The first formed product of the union of glucose, for example, with phenylhydrazine $C_6H_5NH \cdot NH_2$, is a soluble compound called a hydrazone which is represented as follows:¹



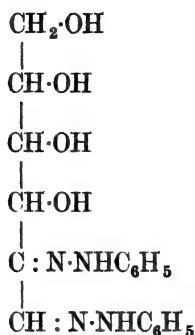
water being formed at the same time.

In the presence of a larger quantity of the reagent a yellow, almost insoluble precipitate of the osazone is thrown down, and

its Davy Medal; he received the Faraday Medal from the Chemical Society on the occasion of his delivering the Faraday Lecture in 1907. He received the Nobel Prize for Chemistry in 1902. For further details of Emil Fischer's life and work, see the Memorial Lecture by Professor M. O. Forster, published in the *Journal of the Chemical Society*, 1920, p. 1157.

¹ No attempt is made here to show the spatial arrangement of the various H and OH groups; see p. 430.

this may be collected, examined under the microscope, and its melting-point ascertained. The osazone is represented by the following formula :



Fructose undergoes exactly similar changes and yields an osazone identical with the compound obtained from glucose. The osazones when heated with a little hydrochloric acid give up their phenylhydrazine, and the resulting compound (called an osone) by the action of zinc dust and glacial acetic acid, takes up two atoms of hydrogen and is converted back into a saccharose. When the original sugar, like glucose, belonged to the aldehyde type of sugar, the product of this change will be a sugar of the keto type ; if, for example, the process starts with glucose the decomposition product of the osazone will be fructose.

The methods used for the synthesis of the natural sugars, as well as of others, containing respectively less or more carbon in the fundamental chain can only be indicated by one or two examples. Of these the most interesting perhaps are those which start from very simple compounds, the synthetical formation of which was long ago established.

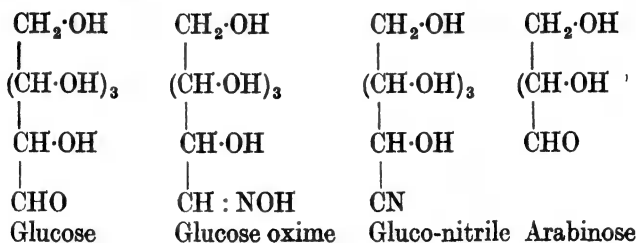
The first case which naturally presents itself is the sugar which has been called *acrose*, and was one of the first produced synthetically by Fischer. Acrolein and its dibromide have long been known ; by treating the latter with baryta a condensation of two molecules into one is brought about, the bromide being eliminated ; $2\text{C}_3\text{H}_4\text{OBr}_2 + 2\text{Ba(OH)}_2 = \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{BaBr}_2$.

From the sugar thus produced others can be obtained as the result of internal changes brought about by methods of which the general nature has already been indicated. α -Acrose appears to be identical with inactive fructose.

To build up a higher saccharose from one containing a smaller number of atoms of carbon a well-known method has been made use of which consists in adding on the elements of hydrogen cyanide to the lower sugar and then splitting off the nitrogen from the resulting compound. Thus glucose $C_6H_{12}O_6$ may be made to yield by a series of steps the heptose or glucoheptose $C_7H_{14}O_7$.

On the other hand, glucose may be deprived of one atom of carbon and the chain shortened down to five atoms by a series of operations which have a certain relation to the above.

By the action of hydroxylamine glucose, like other aldehydic compounds, yields a substance called an oxime, and from this the elements of water may be removed. By further operations the elements of hydrogen cyanide are eliminated. The principal stages are shown below :¹

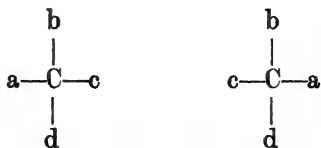


By such means then the monosaccharose group has been extended so as to include members containing from two to nine atoms of carbon with constitutional differences corresponding to the glucose or aldehydic type and the fructose or ketonic type. The actual number of individuals recognised and characterised is, however, very much larger than might be inferred from such a simple statement. To realise the great extent and the complicated nature of this field of enquiry it is necessary to remember that the majority of these substances rotate the plane of the polarised ray, and that this property is traced to the presence in each molecule of several asymmetric atoms of carbon. The general nature of this conception has been already explained, but the case of the sugars requires a little closer examination.

Imagine a single atom of carbon united with four other atoms or groups of atoms all different. These may follow one another,

¹ See footnote, p. 433.

projected on the plane of the paper, in either of the two ways shown below, that is in the direction in which the hands of a clock move or the reverse.



It is obvious that these two arrangements are such that the one is a mirror-image of the other. If but one atom of carbon in this condition is present in the compound there may be two varieties of the same which agree together in all chemical characteristics, and, generally speaking, in all physical characters except one, and that is in their action on the polarised ray. One will rotate the plane to the right, the other to the left through the same number of degrees. But if a pair of compounds, both being alcohols or acids or aldehyds or ketones, etc., contain two asymmetric atoms, then there will be a pair of stereoisomerides, one dextro- and one lævo-rotatory, while there will be a third substance which will be optically inactive. Now in a saccharose with a chain of six carbon atoms, of which glucose is an example, there are actually four asymmetric carbon atoms; there must then be, according to the hypothesis, eight stereoisomeric forms with right-handed rotation and eight others with equal left-handed rotation. Most of these compounds are actually known, though only a small proportion of them occur in nature.

Though practically identical in respect to chemical reactions a very important difference is observed in their physiological relations, for they are acted upon very differently by yeast and other ferments. Thus the two components of invert sugar, glucose and fructose, are fermented into alcohol and carbonic acid at different rates, and while *d* glucose is fermentable *l* glucose, its optical isomeride, remains unaffected. In fact, it is in general only the dextro-forms among the hexoses which are capable of entering into fermentation. The majority of the saccharoses containing less and more carbon are unfermentable. These facts are difficult to account for, except on the assumption that there is a relation of spatial structure between the sugars and the enzymes, which appear to be the agents in the fermentive process, which has been compared to the interaction of lock and

key. There is considerable evidence that in the first stages of fermentation there is production of compounds into which the molecule of the sugar enters, and, in fact, a hexose phosphate— $C_6H_{10}O_4(H_2PO_4)_2$ —has actually been isolated.

The whole process, however, is still imperfectly understood and will continue to furnish problems for research. Changes of a kind similar to those which go on in fermentation probably occur in the tissues of both animals and plants, and the subject is one which is of great importance in physiology.

CHAPTER XXIX

PROTEINS OR ALBUMINOUS SUBSTANCES

THESE are slimy, glutinous, or gelatinous substances which form the basis of the animal body, and which also occur in the juices of vegetables.

Chemists and physiologists between them have been so busy that they are able to distinguish and characterise some fifty substances which are gathered under this name. Some of these are familiar enough in white of egg, in the serum of blood, in milk, in animal cartilage, bone, and horn, in the gluten of wheat flour, and in many seeds such as peas, beans, and nut kernels. They are all, as found in nature, mixtures of highly complex compounds containing the elements carbon, hydrogen, nitrogen, oxygen, usually sulphur, and sometimes also phosphorus and iron.

The study of these compounds has been proceeding, it may be said, long before systematic chemistry began, for some of the old chemists two hundred years ago learned to recognise a chemical difference between substances of this kind which are particularly characteristic of animal matters, and the materials of which wood and vegetable tissues chiefly consist. When the former are subjected to heat, and are destructively distilled, they yield a foetid liquid which smells ammoniacal and acts like an alkali on test paper. Wood and vegetable matter, on the other hand, give an acid distillate. But such insight as the chemical physiologist now enjoys into the constitution of the proteins is the result of researches which have been accomplished almost entirely within the last forty years.

The early days of organic chemistry were associated almost exclusively with the study of medicine and biology. This was natural owing to the readiness with which definite crystalline principles were obtainable by easy processes from plants and from animal matters. Nearly all the operations undertaken down to the beginning of last century had some practical utilitarian object, such as the production of dyes or tanning materials, the processes of fermentation, the distillation of spirits, the examination and preparation of drugs. It was only in the hands of a few of the older chemists that organic matters were examined with the primary object of ascertaining something as to their nature. When, however, such a man as the Swedish Scheele (1742-1786) entered the field discoveries were made so rapidly that it appears almost surprising that his example was not followed more freely by others. There were, however, two great difficulties in the way, the one was the lack of methods by which the composition of such compounds could be accurately determined, the other was the absence of the fundamental ideas which would enable the results of such analysis to be interpreted. The latter was provided in due time by the application of Dalton's Atomic Theory (1808), but it was much later before the methods of organic analysis were devised and perfected by Liebig.

But even before the advent of the Atomic Theory many definite substances had been extracted from natural sources. Citric, tartaric, malic, lactic acids were known, urea and uric acid, asparagine, morphine from opium, and glycerine by saponification of fats, beside hydrocyanic acid and many other carbon compounds. These, however, were isolated examples of naturally occurring principles, and their relations to one another or to the animal or vegetable sources from which they were extracted or to any system of things had yet to be discovered. One of the first important steps was taken when in 1828, Wöhler found that the inorganic salt ammonium cyanate by mere evaporation of its aqueous solution was transformed into urea by a rearrangement of its elements without loss or gain of any constituent. Changes of this kind now excite very little surprise. Scores of metamorphoses of a similar character are now known, and in the years which have elapsed since Wöhler's time hundreds of chemists have been busily at work. It is estimated that about 250,000 distinct carbon compounds are now known. These great

advances, including the remarkable department of stereo-chemistry (chapter XI), which has sprung into existence within the last sixty years, are the natural outcome of the pursuit of knowledge for its own sake. Similar advances have been recorded in other branches of science on the recognition of the same principle. But the time has arrived long ago when the systematisation of the vast mass of knowledge acquired concerning the origin, synthesis, and properties of carbon compounds may be turned to account in the endeavour on the part of physiologists to penetrate some of the mysteries connected with living things. This has become imperatively necessary not only in the practice of medicine, to which the organic chemist has supplied so many now indispensable medicaments, but for the better understanding of the processes which go on in the body, in health as well as in disease. Nor is this knowledge applicable only to the human and animal body. Vegetable physiology brings to the agriculturist a practical assistance which enables him more successfully to cultivate his land, to understand the application of manures and the rotation of crops, and generally to gather from the soil a larger yield of food stuffs of all kinds.

But in order that all these applications of chemical knowledge may be accomplished the knowledge itself must be stored up and made accessible. To this end the chemist must study carefully and record fully the composition and properties both physical and chemical of a very large number of compounds.

It has already been pointed out in the chapter on sugars that not only is the proportion of carbon, hydrogen, and oxygen present in these compounds a matter of importance, but the number of atoms which enter into the molecule and the configuration of the molecule, that is the arrangement of the atoms in space, determine the part which these substances play in the vegetable and animal economy. Two sugars may have exactly the same composition and molecular weight and yet the one will have a more decided sweet taste than the other, the one will be resolved into alcohol and carbonic acid by the action of yeast, while the other will not. But though the chemist can in the laboratory build up from the elements carbon, hydrogen, and oxygen, compounds identical with those which are provided for us by nature in the plant, the physiologist cannot as yet form more than rude conjectures as to how they are generated in the plant.

The first step in the construction of the tissues of the higher plants consists in the decomposition of carbon dioxide derived from the air in the green parts of leaves and stems under the stimulus of the sun's rays. But how this comes about no one knows, and there is difference of opinion even as to the nature of the first product of the fixation of the carbon and rejection of the oxygen which is known to go on. The case is still more difficult when an attempt is made to conceive how protein matters are formed which require the co-operation of nitrogen, sulphur, and phosphorus derived from mineral compounds of these elements brought up from the soil. It is the first step which causes the chief difficulty; once a molecule is formed of the kind which has been described as a protein, even of the very simplest kind, the attachment of a number of similar molecules may conceivably lead to the formation of the complex albuminous matters which are so intimately concerned in the affairs of the living tissue. Some indication of the mode of attachment of the simple molecules to form the complex proteins has been obtained from the chemical studies which will always be associated with the name of Emil Fischer.

The large number of apparently distinct compounds, presenting as they do few of the characters by which pure chemical individuals are usually recognised, renders the investigation of the proteins one of the most difficult tasks undertaken by the chemist. An attempt has been made to classify these substances, and provisionally we may accept the scheme which is given below; although it has many limitations it has been found useful. This scheme is the result of the work of a Committee of the American Society of Biological Chemists (1908), and is very similar to one proposed by the Physiological Society in England. It includes vegetable as well as animal proteins.

I. The Simple Proteins.

- a.* Albumins.
- b.* Globulins.
- c.* Glutelins.
- d.* Prolamins.
- e.* Scleroproteins or albuminoids.
- f.* Histones.
- g.* Protamines.

II. Conjugated Proteins.

- a. Nucleoproteins.
- b. Glycoproteins.
- c. Phosphoproteins.
- d. Hæmoglobins.
- e. Lecithoproteins.

III. Derived Proteins.

1. Primary Protein Derivatives.
 - a. Proteans.
 - b. Metaproteins.
 - c. Coagulated Proteins.
2. Secondary Protein Derivatives.
 - a. Proteoses.
 - b. Peptones.
 - c. Peptides.

The *simple proteins* and the *conjugated proteins* are all substances which are supposed to exist in the tissues and juices of animals and vegetables. They are separated by taking advantage of their solubility or insolubility in saline solutions, such as aqueous ammonium sulphate or sodium chloride, or in alcohol of different strengths. They are all substances which present more or less decidedly an "amphoteric" character, that is they have the power of uniting either with acids or with bases owing to the presence in them of carboxylic groups, $-\text{CO}\cdot\text{OH}$, or amino groups, $-\text{NH}_2$. Since the proteins have the properties of lyophilic colloids in solution (chapter XXIII) their molecular weights are not known accurately, but the values are certainly very great.

The composition of serum albumin, which may be regarded as typical, and so far as percentages of the elements are concerned, is closely similar to other albumins. One estimate is as follows :

Carbon	53.08 per cent.
Hydrogen	7.10 "
Nitrogen	15.93 "
Sulphur	1.90 "
Oxygen	21.99 "

From various considerations a formula has been calculated,



which corresponds to a molecular weight 10,176, but as recent work has suggested a molecular weight of over 40,000, the molecule of albumin must be even more complex than that just depicted. Very little importance can be attached to such expressions, they only serve to indicate a recognition of the highly complicated character of the molecule.

Many of these compounds are coagulated by heat and are precipitated from solution in water, in the form familiar enough in white of egg, as a kind of network of films and fibres which are not reconvertible into the soluble form. The albumins are also precipitated by the addition to the aqueous solution of the strong mineral acids and by the salts of practically all the heavy metals. The precipitate in each case consists of a compound or mixture of compounds of the albumin with the acid or salt used.

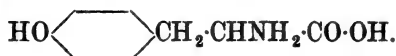
A curious point about the albumins is the fact that they are optically active and that they all rotate the polarised ray to the left. In the case of the sugars it has already been mentioned that the most physiologically active and fermentable rotate the ray to the right.

Conjugated proteins consist of one or more molecules of albumin associated with some other substance of a different nature such as sugar. They do not always contain sulphur, but phosphorus is in many of these compounds a prominent constituent. Several, such as hæmoglobin, the red colouring matter of blood, contain iron.

The *derived proteins* represent the first stages in the process of degradation which the proteins, simple or conjugate, undergo in contact with almost any reagent. Indeed the process of extraction which involves any change in the composition of the fluid in which the natural albumin is normally found probably produces some modification. The solubility is affected even by the comparatively simple operation of diffusion by which the sodium chloride or other saline component of the albuminous fluid is removed. Contact with acids causes incipient hydrolysis, and the same effect is induced by alkalis, by metallic salts and probably also by the enzymes concerned in the process of digestion in the stomach. The products, called albumoses and peptones, are very nearly allied to the albumins and answer to many of the chemical tests which are supposed to characterise those bodies. They are also of high molecular weight. More severe treatment with hydrolysing agents leads to a break up of these compli-

cated molecules, and the products are for the most part comparatively simple. It is of course significant that these products of hydrolysis consist principally of substances generally known as amino-acids.

One of the first cases of the kind was observed by Braconnot over one hundred years ago in the production of what was then called "gelatine sugar" or the "sugar of glue," glycocoll (from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, sweet; $\kappa\acute{o}\lambda\lambda\alpha$, glue) in allusion to its sweet taste. This substance which is now called glycine is amino-acetic acid $\text{CH}_2\text{NH}_2\cdot\text{CO}\cdot\text{OH}$. Two similar substances, namely, alanine or amino-propionic acid, $\text{CH}_3\cdot\text{CHNH}_2\cdot\text{CO}\cdot\text{OH}$, and leucine or aminocaproic acid, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHNH}_2\cdot\text{CO}\cdot\text{OH}$, have also been obtained as common products of this kind of change. Tyrosine has also long been recognized among these products; it is phenyl-*p*-hydroxy- α -amino-propionic acid.



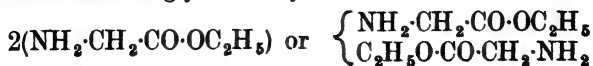
Other more complicated substances are also found among the products of disintegration of proteins, but they almost all partake of the same character and behave as amino-acids.

These facts furnished the principal clue to the mystery of the constitution of olbuminoid substances generally, and led to the remarkable achievements in the direction of their synthesis which we owe chiefly to Emil Fischer and his school. The assumption is that the peptones are constituted of amino-acid groups, and that the number of such residues joined together in the molecule of the protein is relatively small. This view has been practically established by the production of a number of compounds, called by Fischer *polypeptides*, which in many respects resemble the natural peptones.

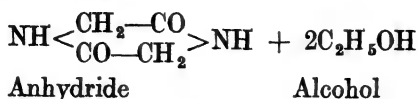
The simplest of the peptides is glycyl-glycine which, containing the residues of two amino-acid groups, is called a dipeptide. Others containing three, four, or many such residues are named respectively tri-, tetra-, and poly-peptides.

Glycyl-glycine is obtained as follows: α -amino-esters, when heated, part with the elements of alcohol and a closed-chain anhydride is formed, thus:

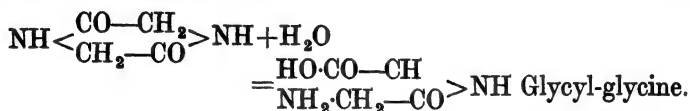
Two molecules of glycine ethyl ester



yield, by loss of H from the NH_2 in one molecule and $\text{C}_2\text{H}_5\text{O}$ from the other molecule,



When the anhydride is warmed with hydrochloric or hydrobromic acid or with dilute alkali, the elements of water are taken up and the dipeptide results; thus



A step by which the higher stages of condensation are reached consists in first forming a compound of the lower peptide with the chloride of an acid radica, such as acetyl chloride, containing an atom of halogen, e.g. chloracetyl chloride $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{Cl}$. In such case HCl is eliminated and a compound is formed which, by the action of ammonia, exchanges Cl for NH_2 and the polypeptide results. Thus glycyl-glycine gives chloracetyl-glycyl-glycine



which yields diglycyl-glycine (a tripeptide)



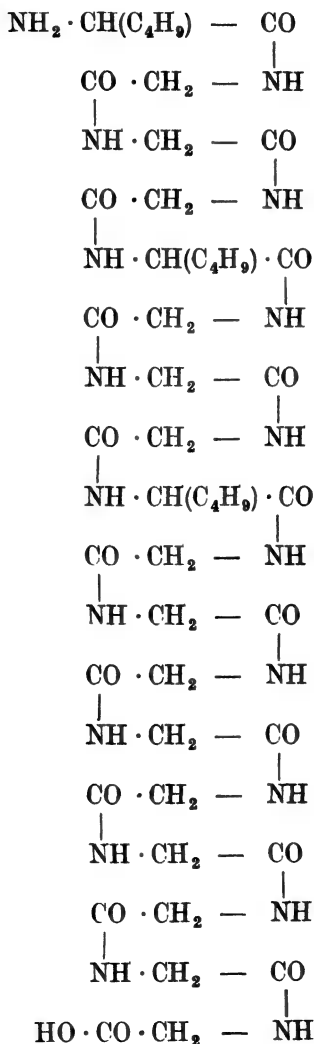
Proceeding on similar lines more complex molecules are built up by making use of other amino-acids, such as aspartic acid,



the acid derived from asparagine, a crystalline, soluble amide which occurs commonly in plants. Aspartic acid is also found among the products of the degradation of proteins.

More than one hundred of the artificial polypeptides have been produced by similar methods. Fischer has described the preparation of an octo decapeptide, derived from fifteen molecules of glycine and three molecules of *l*-leucine, which in its external properties closely approaches many natural proteins. Thus penta glycyl glycine was allowed to react with *d*-bromo-*iso* capronyl diglycyl-glycyl chloride and the product so obtained was treated with ammonia with formation of *l*-leucyl octoglycyl

glycine. By a repetition of this series of reactions the octo decapeptide, *l*-leucyl triglycyl—*l*-leucyl triglycyl—*l*-leucyl octoglycyl glycine is produced. The formula of this is given below.



A polypeptide containing still one more amino-acid unit was synthesised by Abderhalden and Fodor in 1916; this differed

from the one already described by the introduction of an additional *l*-leucyl radical, $\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}$, between the sixth and seventh radicals from the bottom in the structural formula shown.

This array of symbols, formidable as it appears, is evidently only that of an amino-acid of which the amino group is at one end of a long chain, while the carboxyl group is at the other. In examining this formula it must be remembered, however, that the zigzag representation has been adopted merely for convenience; actually the configuration of the molecule will probably be quite different, because of the spatial arrangement of the groups surrounding the carbon and nitrogen atoms (see chapter XI). Complicated as is the representation on p. 445 this is simple in comparison with that which would have to be used for an actual protein; the molecular weight of Abderhalden's polypeptide is only 1326 in comparison with the many thousands of a protein.

Until recently it was generally accepted that the carbon and nitrogen atoms in a protein were in a continuous chain, but evidence has now been brought forward which suggests that closed chains or rings are present. This subject is still a matter for discussion and argument.

Emil Fischer has given a clear account of his work in the Faraday Memorial Lecture of 1907, delivered in accordance with custom, in the lecture theatre of the Royal Institution in London. "Of the numerous attempts to unravel the constitution of the proteins by analytical means," he said, "the only method which has given useful results hitherto is that of hydrolysis. Hydrolysis can be effected by acids or by alkalis and also by digestive enzymes, the products as is well known, besides ammonia, are albumoses, peptones, and ultimately amino-acids. The wide range of variation in composition of these amino-acids is illustrated in the following table :

Glycine	(Braconnot, 1820)
Alanine	(Schützenberger, Weyl, 1888)
Valine	(v. Gorup-Besanez, 1856)
Leucine	(Proust, 1818 ; Braconnot, 1820)
<i>iso</i> Leucine	(F. Ehrlich, 1903)
Phenyl-alanine	(E. Schulze and Barbieri, 1881)
Serine	(Cramer, 1865)
Tyrosine	(Liebig, 1846)

Aspartic acid	(Plisson, 1827)
Glutamic acid	(Ritthausen, 1866)
Proline	(E. Fischer, 1901)
Oxyproline	(E. Fischer, 1902)
Ornithine	(M. Jaffé, 1877)
Lysine	(E. Drechsel, 1889)
Arginine	(E. Schulze and E. Steiger, 1886)
Histidine	(A. Kossel, 1896)
Tryptophane	(Hopkins and Cole, 1901)
Diaminotrihydroxy- dodecanoic acid	(E. Fischer and E. Abderhalden, Skraup, 1904)
Cystine	(Wollaston, 1810 ; K. A. H. Möerner, 1899)

“ In this table are included all the substances hitherto prepared from the proteins, the existence of which is established, with a short reference to their discovery.¹ . . .

“ The nineteen amino-acids in the table are the chief hydrolytic cleavage products of the proteins and those which are generally met with. . . . The proportions in which the various amino-acids are obtained from the different proteins vary very considerably. In some cases they are altogether lacking, as may be proved by application of the definite tests for tyrosine, tryptophane, or glycine ; but it is worthy of note that, as a rule, the amino-acids referred to as isolated from the mixtures produced by subjecting albuminous substances to hydrolysis all occur almost without exception ; especially is this true of the important proteins which play the chief part in animal or vegetable metabolism ; so that the conclusion must be drawn that none of them can be dispensed with in organic life. With the exception of diaminotrihydroxydodecanoic acid² they have all been so thoroughly investigated that their structure is well established. The majority also have been synthesised, proof of their structure having, in fact, been given in this way. Only oxyproline, histidine, and diaminotrihydroxydodecanoic acid remain still to be synthesised.

¹ This was in 1907. Since that date further progress has been made in the isolation of amino-acids from proteins ; a few others appear to have been identified, whereas doubt has been cast on the diaminotrihydroxydodecanoic acid mentioned by Fischer, so that some twenty-one or -two are now regarded as established definitely. It is doubtful if many more will be discovered.

² As mentioned in the previous footnote, the existence of this substance is doubtful.

“ With the exception of glycine all the amino-acids derived from natural sources are optically active ; but when prepared by ordinary synthetic methods, as is well known, they are obtained in the first instance in the racemic form. The resolution of the racemoids into their optically active components has been effected quite recently in most cases. Asparagine, however, which is closely related to aspartic acid, had been resolved into the two active forms by recrystallising the inactive synthetic product from water, and separating the two constituents mechanically. Moreover, in the case of some other amino-acids, for example leucine, the antipode of the natural form had been obtained by partially fermenting the synthetic product with moulds. The complete synthesis of the active amino-acids which are obtained from natural sources was first accomplished by the method I introduced based upon the use of the acyl derivatives. The method has been applied with success to the majority of the synthetic products ; its extension to the remaining cases, proline, lysine, tryptophane, and cystine, is not likely to be attended with any difficulties. The synthetical results are summarised in the following table, in which the inactive products are marked *d l*, and the natural active products are recorded separately :

Glycine	(Perkin and Duppa, 1858)
Alaline <i>d l</i>	(A. Strecker, 1850)
„ <i>d</i>	(E. Fischer, 1899)
Valine <i>d l</i>	(Fittig and Clark, 1866)
„ <i>d</i>	(E. Fischer, 1906)
Leucine <i>d l</i>	(Limpricht, 1855; E. Schulze and Likiernik, 1885)
„ <i>l</i>	(E. Fischer, 1900)
<i>iso</i> Leucine <i>d l</i>	(Bouveault and Loquin, 1905)
„ „ <i>d</i>	(Loquin, 1907)
Phenyl-alanine <i>d l</i>	(Erlenmeyer and Lipp, 1883)
„ „ <i>l</i>	(Fischer and Schöller, 1907)
Serine <i>d l</i>	(Fischer and Leuchs, 1902)
„ <i>l</i>	(Fischer and Jacobs, 1906)
Tyrosine <i>d l</i>	(Erlenmeyer and Lipp, 1883)
„ <i>l</i>	(Fischer, 1900)
Aspartic acid <i>d l</i>	(Dessaignes, 1850)
„ „ <i>l</i>	(Piutti, 1887)

Glutamic acid <i>d l</i>	(L. Wolff, 1890)
„ „ <i>d</i>	(Fischer, 1899)
Proline <i>d l</i>	(R. Willstätter, 1900)
Ornithine <i>d l</i>	(Fischer, 1900)
„ <i>d</i>	(Sörensen, 1905)
Arginine active ; partial synthesis from	
ornithine	(Schulze and Winterstein, 1899)
Lysine <i>d l</i>	(Fischer and Weigert, 1902)
Tryptophane <i>d l</i>	(A. Ellinger and Flamand, 1907)
Cystine <i>d l</i>	(Erlenmeyer, jun., 1903) ”

There can be little doubt that any association of amino-acids could be brought about by application of the existing methods. But to deal with the whole of the proteins will be a gigantic task, and after all it may turn out that the natural proteins do not occur singly, but quite possibly are generated in the living tissue two or more together, and that metabolic changes in the body involve the transformation of several of these complex compounds simultaneously.

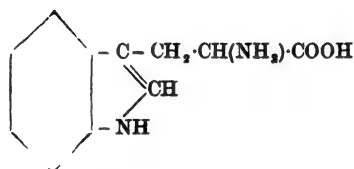
There is evidently much work yet to be undertaken by the chemist and physiologist.

The study of nutrition, at any rate from the chemical side, has already made some progress, but the proteins of the animal body are very numerous and very diverse, and it is at present uncertain how many even of those which are known are necessary for the accomplishment of healthy normal changes in digestion, and in the building up of new tissue. It is interesting to learn from the researches of Abderhalden that a mixture of amino-acids alone without polypeptide is capable of maintaining life, that is to say that the complex proteins of food are not indispensable, and an animal can be kept in health when supplied with the products of their hydrolysis, combined only with suitable amounts of pure fat, starch, cane sugar, and the necessary inorganic salts and vitamins.

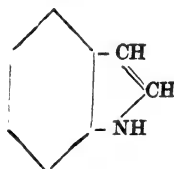
Of the twenty-odd amino-acids present in proteins it appears that at least four, namely, tryptophane, lysine, cystine, and histidine, and possibly some or all of four others, arginine, proline, tyrosine and phenyl-alanine, cannot be synthesised by the animal organism. It is essential, therefore, that these should be supplied, either in their simple form, or else combined as polypeptides or

proteins, in order that growth may continue. Given this relatively small number of amino-acids the body can make all the others it requires. The inferior food value of gelatine is explained by the fact that it is a protein containing neither tryptophane, cystine nor tyrosine, and only very small traces of histidine.

An interesting account of the work showing the essential nature of tryptophane in the diet is given by Professor (now Sir) Frederick Gowland Hopkins, in a lecture to the Chemical Society delivered on May 18th 1916, (*Transactions*, p. 629). Tryptophane has the formula :



and this includes the indole ring :



which is characteristic of several excretory products, and which the animal body does not seem fitted to produce from other materials. The unpleasant odour of putrefying protein is attributed to indole and its derivatives.

Even at the present early stage of the development of the subject some practical lessons may be learned. Among these it is evident that one kind of protein-containing food cannot be substituted for another indiscriminately.

To borrow the language of Saint Paul: "All flesh is not the same flesh; but there is one kind of flesh of men, another flesh of beasts, another of fishes, and another of birds." This is true in strict biochemical sense, and it is no less true that a diet which will maintain one person in health would not be suitable for every individual of the same race. Probably the safest plan is to include a variety of protein in the diet.

Of late years a number of materials under fanciful names have been offered to the public as possessing extraordinary

nutritive qualities. The phospho-proteins are specially valuable in promoting the growth of young animals, and as they are present in milk, preparations made from curd have a certain value.

Yeast from the brewery is another material which is turned to account in the production of food. Dry yeast contains about half its weight of proteins, and without preparation it may be used advantageously as a cattle food. A product made from it by a patented process closely resembles extract of meat, and may be used in a similar way.

CHAPTER XXX

NATURAL COLOURS

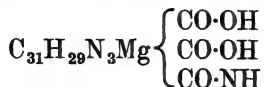
THE vegetation which clothes so large a part of the earth's surface, though differing so much in form, height, structure, and general character from the tropics to the limits of temperate zones, agrees in one character, namely, the colour of the foliage when young and active. This green colour is found in nearly every species of plant, the fungi being the most important exceptions; it is in practically all cases due to the presence of a substance named *chlorophyll*, literally the green of the leaf (*χλωρός*, grass green, *φύλλον*, a leaf). This is deposited in the form of irregularly shaped granules contained within the cells of the leaf and other green parts of a plant. By viewing under the microscope a thin section of any such part it will be seen that the chlorophyll grains are chiefly found in the cells which lie just beneath the surface of the leaf. As a rule this substance is only formed in the presence of daylight, and its production is greatly accelerated by direct sunlight. When a plant is allowed to grow in the dark the chlorophyll is suppressed and the result is the familiar "blanching" which is commonly practised by the gardener. The production of the green colouring matter is intimately associated with the development of many characteristic vegetable principles, such as essential oils, bitter and flavouring substances, as may be noticed in the blanched stems of celery, sea-kale, leek, etc. Its relation to the production of starch is of the utmost importance in vegetable physiology, as

starch is usually first formed within the chlorophyll granules and is probably formed by them or with their indispensable assistance directly from atmospheric carbon dioxide. It appears from experiments made by Pfeffer long ago that when plants are kept in an atmosphere entirely deprived of carbon dioxide they form no starch, even in strong sunlight.

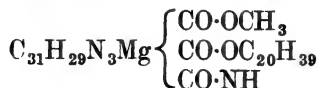
It is not, however, in the explanation of how starch is produced in the plant nor in the origin of chlorophyll that advances of special interest have been accomplished within recent years, but in the practical solution of the question as to the composition and constitution of this green pigment. The problem is not new to chemists. For the greater part of a century attempts have been renewed many times to devise a method by which chlorophyll can be extracted from green leaves without altering it in some degree by the action of the solvents employed for the purpose. Dr. Schunck of Manchester, about forty years ago, supposed that he had succeeded in isolating pure chlorophyll, and he prepared from it a series of crystalline derivatives. By the action of alcoholic potash he obtained a compound which he called phyllotaonine and a derivative of this named phylloporphyrin. The latter was found to have an absorption spectrum nearly allied to that of hæmoporphyrin, a derivative of the colouring matter of blood. In these researches he was joined by the Polish professor, Marchlewski. The formula they proposed was, however, not confirmed by the later researches of Willstätter, to whom we owe the greater part of the knowledge we now possess of the composition and products of decomposition of this important substance.

As a result of the very careful work of Willstätter and Stoll, between 1906 and 1913, methods were devised for extracting the green plant pigments without altering them chemically; two distinct, but closely related substances, were found to be present which were called chlorophyll-*A* and chlorophyll-*B*. Both were very complex compounds containing magnesium and their formulæ were represented by $C_{55}H_{72}O_5N_4Mg$ and $C_{55}H_{70}O_6N_4Mg$, respectively, the latter containing two hydrogen atoms less and one oxygen more than the former. In most plants the ratio of the two chlorophylls is about three parts of *A* to one part of *B*, but in certain algæ the amount of chlorophyll-*B* is very small. Most of the investigations on the chemical structure of the green plant colouring matters have been devoted to

chlorophyll-*A*, for once this is known that of the *B* compound will be derived from it. Chlorophyll-*A* is the methylphytol ester of a tribasic acid to which the name chlorophyllin has been given with the formula : ¹

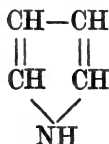


The full formula of chlorophyll-*A* is therefore :



Phytol is an unsaturated alcohol, $\text{C}_{20}\text{H}_{39}\text{OH}$, which in the isolated state is a colourless oil boiling at a high temperature, and any attempt to distil it, except in a vacuum, leads to its destruction.

The colour appears to be connected with the complex nitrogenous nucleus, and the magnesium is supposed to be united in a peculiar manner with the four nitrogen atoms. Treatment of chlorophyll with alkaline reagents fails to disturb the magnesium, but it is extracted and removed by the action of acid liquids. The nitrogen atoms are believed to exist in the molecule of chlorophyll in the form of closed chains constituted in the same manner as in the compound known to the chemist as pyrrole :



In the derivatives of chlorophyll some of the hydrogen atoms are replaced by methyl, CH_3 , or ethyl, C_2H_5 , or more complex groups.

One of the most interesting facts in connection with this enquiry is the discovery that hæmoglobin, the red colouring matter of blood, yields by chemical decomposition compounds having the same fundamental structure.

There is thus a near relationship between hæmoglobin and

¹ For a valuable, although highly technical, summary of recent work on chlorophyll, see an article by K. F. Armstrong, *Chemistry and Industry*, 1933, p. 809.

chlorophyll, with one important difference. It has already been mentioned that chlorophyll contains magnesium attached to the nitrogen atoms. Hæmoglobin contains iron in a similar position. The presence of small quantities of a metal as an essential constituent of these colouring matters is a point of considerable interest, and though of much smaller importance a very curious instance is found in the wing feathers of certain birds which contain not iron but copper. The red colour exhibited by a number of African birds, called Turacos or Plantain-eaters, was examined by the late Sir Arthur Church in 1869, and found to be due to a pigment which he called turacine, which contained some 8 per cent of copper bound up with a nitrogenous structure.

It appears that turacine is actually a cupriferous derivative of hæmatoporphyrin which may be regarded as essentially the colouring matter of blood deprived of its iron. How the birds acquire the copper found in their feathers is not clear, but the same remark would apply to the minute quantity of other elements found in the tissues of animals and plants, the fluorine, for instance, found in the bones and teeth. The papers relating to turacine make no mention of the blood of the birds in whose feathers this red colouring matter is found; presumably the blood contains only iron as in all other cases.

At one time doubt was expressed whether the chlorophylls obtained from different plants were identical; it seems now, however, to be generally accepted that all the chlorophylls are fundamentally the same, although the relative amounts of the *A* and *B* may vary in different plants. It has been recently suggested by Professor Conant, in America, that there are two isomeric forms of chlorophyll-*A*, that is two substances having the same ultimate analysis but with the constituent elements arranged in a slightly different manner; it is possible that the relative amounts of these two forms, if present, may also differ from plant to plant.

In view of the general prevalence of chlorophyll and the change of the green bud into the coloured flower as well as the frequent tendency to reversion of coloured parts to the green state, it might be supposed that the various bright hues of flowers were produced by some kind of chemical transformation of chlorophyll. This idea was certainly accepted at one time, but it appears to be without foundation.

Many vegetable colouring matters were extensively used as dyes before the discovery of the coal-tar colours, and a few still retain their position. It is only necessary to remind the reader that, notwithstanding the advent of the very numerous synthetic dyes, natural indigo, logwood, safflower, and madder colours are still used to a small extent in some places, and that the colouring matters of the damask rose, the red poppy, turmeric root, litmus, and red cabbage are employed in other ways. The diversity of natural colouring matters is a very interesting fact. In many cases it is probably true that the accumulation of colouring matter, especially in the coverings of the flower, is connected with a definite advantage to the plant. The bright coloured corolla, often associated with the secretions of essential oil which fills the surrounding air with perfume, brings the visits of insects which in many cases play an essential part in the process of fertilisation. On the other hand, there are many coloured substances secreted in the inner parts, in woods, like the barberry and logwood, in roots, like the turmeric and rhubarb, in bark, as in the quercitron (*Quercus tinctoria*), in berries, such as those of buckthorn and various other species of *Rhamnus*. In such cases the advantage, if any, must be of a different kind. It seems probable that, in many cases at any rate, the colouring matters thus deep-seated are, like many of the other chemical compounds found in the tissues of plants, merely waste products concomitant with those which must be regarded as essential.

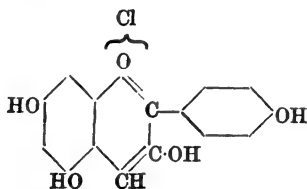
A plant requires, for example, to manufacture the chemical compound cellulose of which the membranous walls of its cells and vessels are composed, and in wood these are thickened and strengthened by encrusting deposits of similar material.

Cellulose is a carbohydrate and may conceivably be formed by condensation from other carbohydrates, the sugars and starch, which are among the first, if not the very first, compounds built up from the elements of water and carbon taken from the carbon dioxide of the air. But these synthetic operations are only affected through the agency of the complex mixture of nitrogenous substances contained in the protoplasm, which are themselves constantly in process of formation and decomposition.

In these highly complicated chemical changes by-products are doubtless formed, and unless they are utilised for some purpose in the plant itself they may accumulate in the tissues and

may even obstruct the processes of growth. Such deposits are sometimes mineral, as in the deposits of phosphate of lime in teak, sometimes resinous, as in the heart wood of many trees, sometimes in the form of alkaloids, such as quinine, which are found in the bark. These by-products may be compared to the chips and shavings which collect in a carpenter's shop, but which have no relation to the form or purpose of the object which occupies his labour.

Nearly all the blue, violet and red colours of flowers, fruits, leaves and other parts of plants, consist of substances called *anthocyanins*. These exist in the plants in the form of glycosides, and so may, therefore, serve to some extent as stores of nutriment available during the process of fertilisation and development of the ovary. The colouring component, which is associated with the glucose or other sugar, is called an *anthocyanidin*, and it exhibits a certain degree of basic character as it combines with the elements of acids. These colouring matters contain no nitrogen, but only carbon, hydrogen, and oxygen, and, unlike chlorophyll, no magnesium or other metal. Seven anthocyanidins have so far been isolated, and for our knowledge of their structure we are indebted mainly to the work of Professor Willstätter, whose name has been mentioned in connection with chlorophyll, and of Professor Robert Robinson, of the University of Oxford. They have all been synthesised and shown to be derivatives of the fundamental grouping :



each of the two hexagons representing a "benzene" ring of six carbon atoms (compare p. 311). As already mentioned, the anthocyanidins exist in the plant combined with one or two molecules of glucose or other simple sugar, and consequently the actual number of anthocyanins is considerably greater than seven.

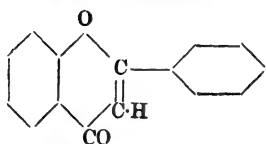
In many cases the red and blue of different flowers appear to be due to exactly the same substance ; for example, the blue of the cornflower (*Centaurea Cyanus*) and the red of the rose (*Rosa*

gallica) are both caused by the substance cyanin, which is a diglucoside of cyanidin. It was thought at one time that the difference in colour was caused by alkalinity in the cornflower and acidity in the rose, since it is known that the anthocyanins show colour variations of this type according to the acidity or alkalinity of the medium ; this view has latterly been shown to be incorrect, since the difference in acidity of the different flowers is quite insufficient to account for the difference of colour. It appears that red is the normal colour, since the flower sap is slightly acid, but that the combination of the anthocyanin with colloidal matter present in the sap results in a blue colour. Other factors, such as the presence of other pigments, of tannins and of iron salts in small amounts, may also result in a tendency towards a blue shade.

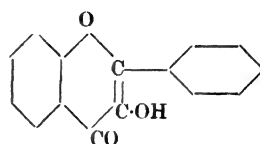
Certain flowers, such as the wallflower (*Cheiranthus Cheiri*), occur in red, brown and yellow varieties ; the red colour is due to an anthocyanin, but the yellow, which mixed with the red produces brown, is caused by pigments of quite a different type. These consist mainly of the substances *carotene* and *xanthophyll*, which Willstätter showed are always associated with chlorophyll in the green parts of plants. Carotene is a hydrocarbon of the formula $C_{40}H_{56}$, and three isomeric forms actually exist in nature ; it is responsible for the colour of the carrot and hence its name. The formula of xanthophyll is $C_{40}H_{56}O_2$; four isomeric forms are known, each of which is a derivative of carotene containing two OH groups in place of two H atoms. Both the colouring matters have been obtained in crystalline form and the basis of their chemical structure has been elucidated ; it is a very striking fact that the skeleton of carbon atoms involved is the same as that of phytol, which is a unit in the molecule of chlorophyll. Carotene and xanthophyll occur in most yellow and orange flowers and fruits ; as already indicated (p. 346) carotene is the precursor of vitamin-A.

Another type of yellow colouring matter occurring in nature, but only rarely in flowers, such as the yellow snapdragon (*Antirrhinum majus*), belongs to the group of substances known as *flavones* or to their hydroxyl derivatives the *flavonols*, in the form of their glycosides. Some of the earliest known natural dye-stuffs, and in fact the most important of this type of dye still in use, belong to these groups of colouring matters ; well known examples are *quercetin*, obtained from quercitron bark or from

Persian berries, which is a flavonol, and *luteolin*, a flavone, which forms the basis of a very ancient dye-stuff extracted from dyer's weed, or wild mignonette (*Reseda luteola*), or from dyer's greenwood, or broom (*Genista tinctoria*). The basic structures of the flavones and flavonols are



Flavone.



Flavonol.

and a comparison with the fundamental grouping of the anthocyanidins, already given, shows the similarity between them. It is fairly probable that these three groups of colouring matters have a common parent in the plant.

Quite distinct from these yellow colouring matters is another group with the similar name of *flavins* (Latin *flavus*, yellow); these substances are very widely distributed, although always in very small amounts, and occur in both animal and vegetable matter. The flavins have a formula approximating to $C_{17}H_{20}N_4O_6$, that is they contain the element nitrogen, and one of them, lactoflavin obtained from milk, is thought to be identical with one of the constituents of vitamin-B (see p. 347).

The story of all these natural dyes would tell, if it could be completely and truly read, how much there is still to learn of nature's secrets. The chemist is just beginning in the twentieth century to find out the mere composition of a few of these dye-stuffs contained in the minute cellular laboratories of the plant, but the materials out of which they are formed and the process by which they are elaborated are alike unknown. From remote antiquity it has been known that solar energy is the source or, at any rate, a condition of all life, but in spite of a great deal of investigation on the chemical action of light the manner in which the plant builds up the complex colours and other products is as much a mystery as ever.

Before leaving the subject of natural colouring matters we may return to a brief survey of some colouring matters of animal origin. Of these the red substance in blood corpuscles is obviously the most important. This exists in the blood in two conditions, according as it is taken from the arteries or from the veins, and

especially after asphyxiation. In the former it is called oxyhæmoglobin, and consists of hæmoglobin combined loosely with oxygen. This power of entering into union with various gases is characteristic of hæmoglobin, and in at least one case, namely, carbon-monoxide, this ought to be borne in mind as it serves to explain the dangerously poisonous effects of breathing an atmosphere containing even a small quantity of that gas.

Oxyhæmoglobin is crystallisable, and the form of the crystals differs in the blood of different animals. Hæmoglobin and its oxidised form both consist of a compound of a protein and a coloured substance called hæmatin, which is said to have the formula $C_{32}H_{30}N_4FeO_4$. If blood is treated with acids the iron is removed from the red colouring matter, and a new substance called hæmatoporphyrin $C_{16}H_{18}N_3O_2$ results. The views of the experts engaged in this interesting problem being still unsettled it is not advisable to attempt in these pages a display of the constitutional formulæ attributed to these compounds. The only point which appears clearly established is the identity of the ultimate pyrrolic products of vigorous oxidation or reduction obtained from the green matter of the leaf, and the red colouring matter of blood. This close similarity of chemical structure has led to speculations as to the changes which must have come about in the early stages of organic evolution. It may be supposed that the common colouring matter prevailing in the protozoa as well as all the early algæ and other organisms living in water was a substance essentially the same as the chlorophyll now prevalent. It must therefore be inferred that at some time, when worms or other creatures of distinctly animal characteristics began to appear, the provision of much iron in the soil or water inhabited by them led to a modification in the composition of the protoplasmic material of their tissues, and the change may have been further promoted by the exclusion of light from their muddy or earthy habitations. Whatever may have been the change of conditions which led to the change of composition from magnesian chlorophyll to ferruginous hæmatin, the retention of the same fundamental atomic structure in the molecules of these two substances, now so widely separated in function as well as in colour, can only be regarded as strongly indicative of a common origin. No other colouring matter found in animal matters has the same importance and interest as hæmoglobin, and in nearly all cases our knowledge of their composition and

properties amounts to very little. The plumage of many birds, the hair of man and many animals, and the skin of large sections of the human race contain a dark or black pigment, but it may be safely said that nothing important is known of the composition of this substance or mixture of substances, or whether, for example, the wool of the negro and the feather of the rook owe their blackness to the same or to different pigments. But the difficulty of investigations of this kind will be sufficiently illustrated by reference to one other pigment of animal origin, and that a familiar one.

Everyone is acquainted with the beautiful water-colour paint carmine, and the red essence of cochineal, which is used in cookery for colouring jellies, etc. The red substance in these cases is derived from the body of the cochineal insect (*Coccus cacti*) which is cultivated in Mexico and in the Canary Islands, collected, dried, and sent into commerce in the form of small silver grey masses about a quarter of the size of small peas. These are the bodies of the females, the males being furnished with wings, and have but a very brief existence after development from the larva. The red colouring matter has been the subject of experiment since 1813 when it was analysed by Pelletier and Caventou, who assigned to it a formula which included the element nitrogen. Arppe and Warren de la Rue examined it again thirty years later and showed that it did not contain nitrogen. Since that time the carminic acid, so named by the last-mentioned chemists, has had half a dozen different formulæ attributed to it, but the formula now generally accepted is $C_{22}H_{20}O_{13}$. It is a crystalline compound and yields well-defined salts, and an examination of its structure by chemical means has shown it to be a glucoside of an anthracene derivative having some features in common with the red dye-stuff alizarin found in the madder plant (p. 326). It is of interest that similar structures are thus found in these red colouring matters of animal and vegetable origin.

CHAPTER XXXI

ENZYMES

THE process by which grape and other saccharine vegetable juices are converted, after much frothing, turbidity, and ultimate clarification, into an intoxicating drink is as old as the history of mankind. But the true nature of the change which goes on was established only after a long controversy, in which the representatives of a purely mechanical or physical theory originated by Liebig were finally defeated by Pasteur, who established the dependence of ordinary alcoholic fermentation on the action of the living yeast cell.

This was seventy years ago, but since that day investigations into the phenomena of fermentation have reached a new stage, in which attention is concentrated on the agents by which the cell accomplishes its own growth and development at the same time that it brings about chemical changes in the surrounding medium. These agents are called *enzymes*, a term which was brought into use so recently as 1878 by the German physiologist W. Kühne.

Enzymes are not organisms like moulds or bacteria, but may be described as unorganised, colloidal, nitrogenous substances universally present in living animal and vegetable tissues and, though lifeless themselves, are at present producible only from living matter. They are distinguished by a remarkable *catalytic* action on carbon compounds, especially carbohydrates, fats, and proteins. Their actions are in some cases selective, but not always, and they are coagulated and rendered inactive by a temperature below that of boiling water.

The general nature of enzyme action will be understood if a few individual cases are described.

One of the earliest to be recognised and one of the most important of these substances is *diastase*. Early in the nineteenth century it became known that an aqueous extract of malt possessed the power of changing soluble starch very rapidly into dextrin and sugar. Payen and Persoz attempted in 1833 to isolate the active constituent of malt, but with no great success. Forty years later O'Sullivan described a method which was as follows: finely ground pale barley malt was mixed with sufficient

water just to cover it, and after three or four hours the extract was separated by means of a filter press. The clear solution was then mixed with strong alcohol as long as a precipitate was formed, and the latter was collected, washed with alcohol, pressed between a cloth, and dried *in vacuo* over sulphuric acid. Prepared in this way diastase is a white powder, easily soluble in water, and possessing the activity of malt extract. It is, however, far from being a pure substance, as it contains a considerable percentage of mineral matter (chiefly phosphate) which is left as ash when the diastase is burnt.

Calculated on the ash-free substance the results of analysis by two different observers are as follows :

	(Lintner.)	(Szilágyi.)
Carbon . . .	46.66 ..	46.80
Hydrogen . . .	7.35 ..	7.44
Nitrogen . . .	10.42 ..	9.98
Sulphur . . .	1.12 ..	1.14
Oxygen . . .	34.45 ..	34.64

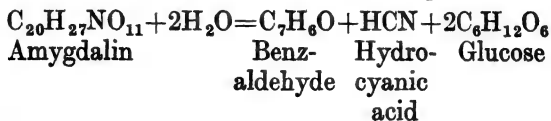
It will be evident on comparison with the analysis on page 441 that this is not the composition of an albumin. It should be added that other analyses have led to different proportions of the elements.

The characteristic property of diastase is its power of converting starch under suitable conditions of solution and temperature into a mixture of maltose and dextrin. Maltose is a relatively simple sugar, somewhat analogous to ordinary cane or beet sugar in its constitution (see p. 428), whereas dextrin is a more complex carbohydrate similar to starch itself.

Diastase, or a substance resembling it in its action on starch, appears to be widely distributed in the vegetable kingdom in leaves and other organs, and it occurs in the grain of all cereals whether raw or germinated.

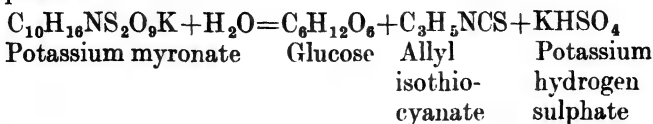
Another interesting case is that of the bitter almond. It must have been known as long as the almond itself that this seed when dry or crushed is without peculiar odour. When strongly pressed both sweet and bitter almonds yield a considerable quantity of a bland fatty oil, which may be eaten as food or used for making soap. If the bitter almond is pounded and mixed with water, a characteristic familiar aromatic odour is developed, which is due to the production of an essential oil which can be distilled off in

steam, and is sold as a perfume and flavouring essence. This substance is benzoic aldehyde, $C_6H_5 \cdot CHO$, and it is well known that in the crude state it is very poisonous, owing to the presence of prussic acid, which accompanies it. These facts were explained by Liebig and Wöhler in 1837. If the cake of bitter almond from which the fixed oil has been squeezed out is exhausted with boiling alcohol a crystalline substance, amygdalin, can be procured from the solution. This is inodorous and almost tasteless, but if mixed with a small quantity of the pulp of *sweet* almonds and water the essential oil is at once developed :



The bitter and the sweet almond both contain an enzyme, or rather a pair of enzymes (amygdalase and prunase) commonly known under the collective term *emulsin*, which together break up the amygdalin in the manner shown in the equation. It would appear in such a case that the amygdalin, the glucoside, and the enzyme are contained in separate cells within the seed. The seeds of many other fruits of the same natural order as the almond, namely, peach, apricot, cherry, etc., as well as the leaves of the common cherry laurel yield essential oil in a similar way.

Another familiar instance of enzyme action is afforded by common mustard. The domestic mustard flour is destitute of pungency so long as it is dry, but when mixed with water the odour of the essential oil becomes apparent almost immediately. Both black and white mustard seed, like the almond, yield by expression a quantity of a fixed fatty oil which has nothing to do with the pungency. The black mustard seed contains a glucoside called sinigrin or potassium myronate associated with an enzyme called *myrosin* contained in a separate system of cells. When crushed with water the glucoside is broken up into glucose, mustard oil (allyl isothiocyanate), and potassium hydrogen sulphate :



A glance at each of the three equations given will show that

the resolution of the glucoside is due to the addition of the elements of water. This is effected by the agency of the enzyme, which in these cases acts as a hydrolysing agent, the chemical compounds which result being the same as those which are commonly produced by dilute acids or alkalis, though of course the *modus operandi* must be different. A hydrolytic action is in fact brought about by the majority of enzymes, but they differ from inorganic hydrolytic agents in the fact that many of them do not carry the process so far as acids do, and also that enzymic action is very often specific. In this last respect, however, they do not seem to differ essentially from some inorganic catalysts, and some of them, emulsin for example, act on a great variety of substances. It would serve no useful purpose in this place to attempt an enumeration of the enzymes mentioned in chemical literature until more has been learnt concerning their composition and the range of their activities. Some of the enzymes which are known to hydrolyse the chief glucosides have already been mentioned in connection with sugar. Two or three may be added which are produced in the animal body and are concerned in the processes of digestion. Ptyalin, secreted by the salivary glands, changes cooked starch, as in food, into maltose and dextrin. Then there is trypsin, which is secreted by the pancreas and causes the degradation of proteins and their derivatives, giving rise to amino-acids and the simpler polypeptides.

Pepsin is contained in the gastric secretion, and papain from the juice of the *Carica Papaya* or Papaw tree is said to have the property of making meat tender. Pepsin acts best in an acid medium such as the gastric juice which contains 0.2 per cent of hydrochloric acid. Trypsin, on the other hand, works best in an alkaline solution such as the pancreatic juice, which also contains several other enzymes.

Among the latter must be mentioned lipase, which splits up fatty matters into glycerin and fatty acid. Other enzymes are secreted by the liver, the kidneys, and the mucous lining of the intestines; their action generally is hydrolytic.

But all enzymes are not hydrolytic in their action. A different class is represented by rennet, which is prepared from the lining of the stomach of the calf and is used for curdling milk in the manufacture of cheese. The clotting of blood is brought about by a similar agent originating under certain conditions in the blood itself and called thrombin.

Yet another class of enzymes possess the power of effecting rapid oxidation, and in reference to this property are called oxydases. The process of oxidation in the tissues is one of great importance for example in connection with respiration, but the mode of action and origin of this class of enzymes is still very obscure, although some striking progress has been made in modern times.¹

The whole subject of enzyme action is so difficult and its systematic study has been undertaken so comparatively recently that only a few generalisations have as yet been recognised.

As to the origin of enzymes it appears that, while they all originate in living protoplasm, they do not exhibit in the early stages of existence the characteristic catalytic actions which later they exercise. In this preparatory condition the substance is called a zymogen; thus pepsin is formed from pepsinogen, trypsin from trypsinogen, etc. In order that an enzyme may become active special conditions and environment, which are characteristic of the particular enzyme, are necessary; in general, the activity is most marked at some definite temperature, over a definite range of acidity or alkalinity, that is of hydrogen-ion concentration, and frequently in the presence of certain salts.

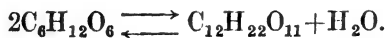
It appears also that in many cases, of which one example, emulsin, has already been mentioned, two enzymes habitually act together to produce the characteristic change, hydrolytic or other, which either enzyme separately is incapable of bringing about or can at most carry partly into effect. An interesting case of this kind has been described by Dr. A. Harden of the Lister Institute, in the study of yeast juice. It was discovered in 1897 by E. Buchner that the cell of the yeast as a whole is not necessary to alcoholic fermentation. By grinding and subsequent filtration a juice may be separated which introduced into a solution of sugar sets up this change. Harden's experiments have since shown that the fermentation of glucose and fructose by yeast juice is dependent not only on the enzyme, zymase, but requires the presence of another substance the nature of which is obscure, but which can be separated by dialysis and withstands the temperature of boiling without destruction of its activity. A phosphate is in addition always necessary. These

¹ See the Fourth Gluckstein Memorial Lecture delivered by Sir Frederick Gowland Hopkins on December 16, 1932, and published by the Institute of Chemistry.

two substances, the enzyme and the co-enzyme are incapable separately of causing alcoholic fermentation.

The co-operation of two colloidal agents in the production of a given effect suggests that there may be bodies which are not mutually helpful, but on the contrary antagonistic. The questions why the blood does not clot in the veins, why the stomach is not itself dissolved by the digestive juices which it generates from its own surface require an answer. This is partly supplied by the hypothesis of anti-enzymes which neutralise the hydrolysing or other action of the enzymes. Thus an anti-thrombin is supposed to prevent the coagulation of the blood while in the vessels by the fibrin ferment or enzyme. Similarly it is assumed that there are antipepsin and antitrypsin which check the action of the pepsin and trypsin in the stomach and intestines. There appears to be, however, some considerable differences of opinion among experts on this question and evidently further investigation is necessary. The relation of antitoxins to toxins is probably of the same character, and the production of "immunity" in respect to certain diseases results from the development in the body itself of some protective substance, or the injection into the body of a serum prepared in the tissues of another animal.

In 1898 the first case of reversible enzyme action resulting in the synthesis of a disaccharose was discovered by Dr. A. Croft Hill. Having observed that the hydrolysis of maltose by the action of the enzyme maltase in yeast was incomplete, he found that starting from glucose alone in strong solution a disaccharose was produced. The substance thus formed by the union of two molecules of glucose was originally supposed to be maltose, but appears to be isomaltose, a sugar obtained by Fischer by the condensing action of strong acids on glucose.



The reversed arrows indicate that the change may proceed in either direction according to the conditions of the experiment. This is in accordance with a very common form of chemical change in which three substances together attain a condition of equilibrium which is disturbed on changing the temperature or altering the proportion of any one of the substances present.

The principle is very important in connection with chemical or biochemical reactions, for it must be borne in mind that in the great majority of cases such a change tends to slacken or to be

stopped altogether if the products of the change are allowed to accumulate. Removal of such products occurs when a gas escapes, or the solution becomes diluted, or any acid or alkali formed is neutralised. In such cases there is no accumulation because the products are removed from the sphere of action or from a condition of activity.

Other cases of synthetical formation of sugars have been observed since 1898, and the reversibility of enzymic action is now well recognised.

The mechanism of enzyme action has received a great deal of attention. How do these complex substances do their work? That in so many cases they are selective in their attitude toward the carbohydrate, protein, or other substance with which they are in contact suggested to Emil Fischer long ago the analogy of the lock and key. When an enzyme finds itself in the presence of two glucoses, for example, having the same composition, molecular weight, and general character, but differing from each other only in "configuration" as indicated by their optical properties, the conclusion seems irresistible that the enzyme is able to fit itself into the body of the one and not into that of the other. This seems to imply that the preliminary to action is a state of union between the enzyme and the "substrate," but the question still remaining is whether this combination is of a chemical nature, or a physical or mechanical nature. In the former case definite proportions would be expected to interact or combine.

The whole subject of enzyme action is, however, still under investigation by a considerable number of chemists and physiologists; in fact it forms part of a new and extensive department of organic chemistry which is usually designated "biochemistry" in allusion to its close association with the phenomena of living beings, vegetable or animal. Any survey of the phenomena exhibited by enzymes cannot fail to excite wonder at the powerful action of these complex and sensitive agents. They are capable of bringing about changes which can be effected by ordinary chemical agents, such as strong acids or alkalis, only under circumstances of considerable concentration or high temperature. The hydrolysis of a fat, for example, can be accomplished either by boiling with alkali, when a soap is produced, or by steam, heated considerably beyond the boiling point of water, when glycerin and fatty acid are produced. The enzyme lipase can

do its work without sensible rise of temperature, and remains active after all is over. Invertase (from yeast), according to O'Sullivan and Tompson, can change 100,000 times its weight of cane sugar into glucose and fructose, and can still go on producing inversion.

In fact the metaphor already made use of to illustrate the specific action of enzymes may be extended a little in order to emphasise the contrast between the operation of these substances and the accomplishment of the same chemical change by ordinary chemical agents. For suppose it is desired to enter a house, the action of the former may be compared to the simple and peaceful process of inserting the right key into the lock, the action of the latter would be more nearly represented by breaking down the door.

The effects described here are nearly all brought about by the enzymes separated from the living tissue in which they were generated. It is usually assumed that their activity and mode of action is the same in the parent tissue, but this assumption, however probable, is incapable of strict verification. In any case it is a matter for further research to what extent the processes of absorption and assimilation, of growth and development are wholly dependent on these catalytic processes, or are at least partly the result of still more complex changes wrought by the living protoplasm itself.

CHAPTER XXXII

ORGANIC CHEMISTRY

IN previous chapters an account has been given of some of the more important constituents of animals and vegetables and of the definite products of secretion. The study of such substances as sugar or colouring matters was formerly called, perhaps not altogether improperly, organic chemistry, as an abbreviated expression meaning the chemistry of organised beings. Such compounds as those mentioned and many others were supposed to be producible only by living things through the agency of what was called *vital force*.

The expression "organic" chemistry has become established

by long usage, and it seems impossible to get rid of it, but it should be remembered that the customary application to the chemical history of all the multitudinous hydrocarbons, alcohols, acids, bases, sugars, etc. etc., is not intended to imply that there is any difference in the fundamental principles of *organic* and *inorganic* or mineral chemistry. A very large number of the known definite organic compounds, in which carbon is the characteristic central element, can now be produced by purely artificial processes in the chemical laboratory, independently of any operation in which plant or animal life is concerned. A considerable number of examples have been mentioned in the earlier pages of the book, and especially in the recent chapters.

So far as animal tissues are concerned the problem of their constitution and how they are wasted and renewed is, from one point of view, simpler than the corresponding problem presented by plants, inasmuch as animals find the materials they require in their food, ready formed in the vegetable matter from which directly or indirectly they derive nourishment. No animal is known to assimilate any element except oxygen from the air, or to build up fats, carbohydrates, or proteins from such simple materials as carbon dioxide, water, and ammonia. The case of the plant is very different. The forest of timber trees equally with the humble moss or lichen with which their trunks are clothed derives the whole of the carbon, which is the chief component of wood, leaves, and fruit, from the carbon dioxide of the air. And this gas is found in the atmosphere to the extent of only 3 to 4 parts in 10,000 under ordinary conditions. How is this accomplished? That is the great problem on which chemists and physiologists have been more or less engaged since chemistry and physiology began. It was proved by experiment two hundred years ago that a willow tree planted in a tub of pure sand and watered with rain water grew and flourished without limit (it actually weighed 60 pounds at the end of the experiment); and though the result seemed to prove, at that time, that vegetable matter consisted only of water, it was shown by later experiments made in the first instance by Priestley, and subsequently confirmed by many other chemists, including Sir Humphry Davy, that the growth is entirely due to the use of carbon derived from the carbon dioxide of the atmosphere. In Davy's Lectures on Agricultural Chemistry given in 1813 he describes experiments in which first a square of turf, and in another case a branch of

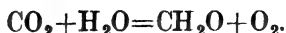
vine, was exposed to an atmosphere containing a large quantity of carbonic acid. Under the influence of sunshine the carbonic acid disappeared and was replaced by oxygen.

It is unnecessary to cite the further experiments of the older observers, but among the many researches in connection with this question which have been recorded during more recent times, there must be mentioned those of Dr. Horace T. Brown published during the years 1893 to 1905 on the nature of the substances formed in the leaf during exposure to sunlight and the rate of decomposition of the atmospheric carbon dioxide. In order that this constituent of the air may come into contact with the active surface it is necessary for it to penetrate into the interior through the small openings, called stomata, which exist for the most part on the lower surface of the leaf, and these minute pores when fully open do not exceed 1 or 2 per cent of the total area of the leaf surface. The astonishing result has been arrived at that in a fully active leaf the atmospheric carbon dioxide is taken up at least fifty times as fast as it would have passed into a series of small openings of equal size with the stomata, if these had been filled with a strong solution of caustic alkali.

The changes which go on in the interior of the leaf are associated in a mysterious way with the green colouring matter, chlorophyll, which plays the part of a sieve or filter of the sun's rays, stopping some and allowing others to proceed.

From the researches of C. A. Timiriazeff, Professor of Botany in the University of Moscow, it has been shown that the reduction of carbon dioxide as well as the production of starch is due to the rays which are absorbed by the chlorophyll. As the chlorophyll transmits chiefly green light the part which is stopped lies chiefly in the red, and on passing through a spectroscope the light which is transmitted is seen to have a dark band between the lines B and C of the solar spectrum. The blue and violet rays produce very little effect.

It is, however, not known with certainty what compound is the first result of the decomposition of the carbon dioxide, though it is commonly assumed that formaldehyde is the initial product. Its formation can be expressed by the simple equation



This accounts for the elimination of the equal volume of oxygen

which is known to be the other product. Formaldehyde is inimical to living organisms, and if it accumulated to any appreciable extent in a living leaf would speedily put an end to all vital processes within ; in other words, it would kill the protoplasm by which it is supposed to have been produced. But it is quite possible that the greater part of it disappears immediately in consequence of condensation into some kind of carbohydrate, which eventually becomes starch and remains stored up for use in the growth of the plant. It is important to note that formaldehyde in the presence of lime or of certain salts of inorganic nature and origin condenses somewhat readily into various sugars, and so here is a process by which it is conceivable that sugars and starches arise in nature.

Theories of this kind have led to various attempts to effect the change by which, from carbonic acid and water, formaldehyde and oxygen are formed, without the aid of the living plant and by the use alone of inorganic materials, the necessary energy required to bring about the reaction being derived from the sun. Several workers have claimed success in their experiments, using colloidal materials as catalysts, but probably an equal number have denied the accuracy of these observations, stating that the formaldehyde obtained in certain cases is to be attributed to the presence of impurities. It is necessary, therefore, to preserve an open mind on this subject ; some eminent scientists are quite sure that formaldehyde is obtained by the action of light on carbon dioxide and water under suitable conditions, whereas others, equally eminent, are just as emphatic in denying this as a proven fact.

In spite of this lack of agreement as to the experimental results it is nevertheless generally accepted as probable that in the plant, under the influence of chlorophyll, formaldehyde in some form is an intermediate product in the building up of starch in the green leaf. There is no doubt that the chlorophyll plays an important part, the exact nature of which is not yet understood. All that can be said at present is that it is not merely catalytic, and that the efficiency of the green matter in association with the living protoplasm in fixing carbonic acid is far greater than that of any combination of inorganic materials yet tried.

Researches of this kind lead to speculations as to the origin of life. Man finds himself in a world so full of miracles, and the daily spectacle is so familiar as almost to paralyse the faculty of

wonder. Nevertheless the desire to form a theory or view as to how it all came about has been in all ages and among all peoples so urgent that in the absence of direct and positive knowledge mythology has always centred round a special act of creation. "In the beginning," when the earth was "void," that is empty, it was filled with all manner of beast and bird and creeping thing, and with the herb and tree which was to be their food. In no case is the nature of the act of creation revealed, or what would be called in modern language the physical or chemical acts or doings by which the water and the dry land were furnished with inhabitants.

Geology assures us that there was a time when the earth was at a temperature at which no living animal or vegetable could exist. There is abundant evidence that as it cooled down it gradually became clothed with a vegetation differing in form and structure from that which now covers its surface, and with a succession of animals of which the earliest were chiefly inhabitants of the water, while the latest of all included man himself.

From these facts and from the knowledge laboriously acquired, chiefly during the last century, concerning the forms, the structure, the habits, and mode of propagation of plants and of animals, the doctrine of organic evolution has arisen, and with slight variation of detail has been accepted by the whole civilised world. This doctrine teaches that the higher animals and plants possessing more specialised organs and internal structure arose from lower, less specialised forms by a process which involved what may be termed experimental trials by Nature, through the results of spontaneous variation and survival of the fittest. The imagination of the naturalist then travels back from mammal to bird and reptile, through fishes and crustacea to sponges and corals, till the animal can no longer be distinguished from the vegetable, and the lowly organism takes the form of an apparently structureless but ever moving mass of jelly. If this is to be thought of as the primal form in which life resided "in the beginning," how did it receive the inspiration which differentiates it from a minute drop of white of egg or gelatinous silica or any similar mass of colloid?

Present views seem to be divided between two opposite camps. On the one hand are found those who cling to the idea that life is a directive influence distinct from any ordinary physical forces, taken either singly or together. On the other hand are the

advocates of the view that all the operations of living beings are the result of physical and chemical processes going on in the organism itself or in response to forces acting on it from the outside.

The adherents of the former view are frequently referred to by those who profess the opposite opinion as "vitalists" and the doctrine as "vitalism" with a tone which seems to imply that such an idea is obsolete. The vitalists do not attempt to explain what life is, but like the rest they are eager to account for the existence of living beings in this world of ours, and to do so must choose between the hypothesis of a special creation and the idea that life has existed, if not in this planet, elsewhere, and that it is as old as matter. To account for its appearance on the earth it would be necessary to make a further assumption. Either we must suppose with Lord Kelvin the arrival of a "seed-bearing meteoric stone" from space outside our atmosphere, the result of the disruption of some other life-bearing planetary body in consequence of collision or otherwise, or the hypothesis of *panspermia* may be accepted. This assumes that the minutest germs of some of the lowest organisms may be small enough to be carried through the cosmical spaces from one world to another, by the pressure of some radiant form of energy.

In either case there remains no problem for the chemist or physiologist to investigate as to the *origin* of life. This problem belongs to the field in which the advocates of the other view have long been at work.

The triumphs of synthetical chemistry during the last forty years which have resulted in the production not only of compounds like formaldehyde containing a small number of atoms and of simple constitution, but substances, especially of the protein class, containing a very large number of atoms and therefore consisting of large molecules, have encouraged the idea that by similar methods substances of still more complex type may be produced which will resemble the natural colloids or even be found identical with them.

In a paper, published in 1913, by the late Professor Benjamin Moore and Mr. T. A. Webster, in which the synthesis of formaldehyde from carbon dioxide and water by the aid of light, in the presence of inorganic colloidal matter, is claimed there appears the following passages :

"Such a synthesis occurring in nature probably forms the first step in the origin of life. . . .

"Without the presence of organic material when life was arising in the world, any continuance of life would be impossible.

"The process of evolution of simple organic substances having once begun, as now experimentally demonstrated, substances of more and more complex organic nature would arise from these with additional uptake of energy. Later organic colloids would be formed possessing meta-stable properties, and these would begin to show the properties possessed by living matter of balanced equilibrium, and up and down energy transformations following variations in environment.

"There can be little question that such energy changes as are above described occur at present, and are leading always to fresh evolutions of more complex organic substances, and so towards life, and equally is it true that they must occur on any planet containing the necessary elements for the evolution of inorganic colloids and exposed to light energy under suitable conditions of environment."

Such statements deserve a close examination. As to the first there will be probably no difference of opinion, for it is obvious that any organism born into a world which contained no organic matter must forthwith perish. But the speculations set forth in the latter part of these conclusions require us to believe that if molecules become big enough they will consequently begin to show signs of life.

What would happen to a very large molecule as soon as it is formed can only be guessed at, and there is absolutely nothing but analogy for guide. It seems agreed that the atoms of elements which attain large dimensions become unstable and in their break-down show the phenomena of radio-activity. But when uranium or radium disintegrates there is, beside a great liberation of energy, the production of two or more substances which obey ordinary physical laws as gas or solid. There is no indication of a return of any part of them to their original state, there is no cycle of events. But, as Sir Humphry Davy is reported to have said, "the substitution of analogy for fact is the bane of natural philosophy."

Chemical synthesis has accomplished some wonderful things by well-known laboratory methods. These methods involve very commonly the use of high temperatures, caustic alkalis,

strong acids, and solvents such as alcohol, ether, or acetone which, at any rate in a concentrated form, never appear among the constituents of either plant or animal. In fact the processes of the laboratory have not the remotest resemblance to those which must be assumed to go on in living tissue.

The chemist can take carbon and hydrogen and by the aid of a high temperature can make them unite together to produce ethylene. From ethylene he can build up tartaric acid by a succession of steps which, however, require the use of chlorine or bromine. The grape-vine also manufactures tartaric acid, but it uses neither a high temperature nor a halogen, and the absorption of carbon dioxide by the living tissue is about fifty times as rapid as its fixation by strong caustic potash, which is practically instantaneous.

The proposition that living matter is being generated afresh during every day of sunshine from mere mineral matter at the present time and through all the past ages of the world since the dawn of life is an assumption which can never be proved. It is also unnecessary if the object were only to account for the continuance of the efflorescence of living forms which cover the surface of the earth. The question to be met relates to the initial act or process by which life was first established on this globe, and to do this it is necessary to recall the conditions prevailing on the earth's surface when in the beginning the globe had cooled down sufficiently to allow of the formation not only of a solid crust, but the deposition of water in the liquid form and its retention at a temperature far below the boiling-point. The materials then available, beside the solid silicates, oxides, carbonates, etc., of the crust, would be water, gaseous oxygen, nitrogen and carbon dioxide, with possibly small quantities of ammonia and sulphuretted hydrogen. Possibly some volatile compound of phosphorus might be formed among the multitudinous products of chemical changes going on, but this would be speedily removed from the atmosphere by oxidation and fixed in the solid crust in the form of phosphate. Among the products formed by the action of water on the silicates and other compounds containing metals there would doubtless be an ample supply of colloidal substances suspended in the waters or deposited in crevices of the crust, and some of these would doubtless be qualified to act as catalysts in promoting the formation of carbon compounds from the carbon dioxide which at that

period would be found as a copious ingredient in the primeval atmosphere. At the time imagined the fixation of the carbon which afterwards took place by the action of vegetation, and its replacement by an equal bulk of oxygen, had not begun. That carbon was afterwards withdrawn and stored up in the beds of coal and in the forests of living trees with which so large a part of the earth is clothed.

Let us suppose that the claims to have obtained formaldehyde by the action of light on carbon dioxide and water in the presence of a catalyst are substantially correct, and that the formaldehyde can subsequently be built up into sugars and starches, then these substances could be brought into existence by the co-operation of the atmosphere, the water, and some colloid constituent of the solid crust. There would thus be provided one ingredient in the dietary necessary for living organisms. But protoplasm is believed to consist of colloid material in which not only carbon, hydrogen and oxygen are elements, but nitrogen is an essential component. Phosphorus is also a constituent of some proteins, and indispensable at some stages of development. Now formaldehyde is a very active substance which readily enters into chemical reactions of all kinds, and it is not impossible that it would react, in the presence of suitable catalysts and under the influence of light, with inorganic nitrogen, in the form of ammonia or nitrates, to yield nitrogen compounds related to those present in living matter. In fact Professor Baly, of the University of Liverpool, has claimed that carbon dioxide and water in the presence of nitrate, when exposed to light, give small amounts of substances which are considered to contain amino-acids and alkaloids. The accuracy of this work has been disputed, but suppose it were correct and that even a complex colloidal protein could be synthesised in this way without the direct intervention of a living organism. We may in the present state of knowledge safely enquire—What then? No chemist will be induced to believe that a pulpy mass of one or more amino-acids, no matter how complex or how associated with saline electrolytes, will cease to exhibit the characters which belong to chemical compounds in general, and acquire of its “own mere motion” the power of utilising and controlling energy, supplied from external sources, in such a way as to give rise to the cycle of events exhibited in every particle of living substance, from the amoeba onwards.

Something has been made of a supposed resemblance between cell membranes and the curious forms which some of the very simplest organisms assume and the films and cavities formed by inorganic colloids in the process of drying, or when in contact with other matters in a different state of hydration. There is just as much resemblance in such cases as is to be found between the forms of fossil plants in the more ancient rocks and the foliaceous tracery produced by frost on the pavements in winter. It has even been suggested that some of these impressions in the palæozoic rocks may after all have been left by frost, and not by the fronds of ancient ferns. No one, however, supposes that if it were so these forms represent the beginning of life.

But protoplasm cannot be thought of merely as a solution of mixed colloids and saline electrolytes. It must consist of aggregates or clusters of molecules of various dimensions and possessing a consistency which no solution could show, inasmuch as a solution would possess viscosity and cohesion equal in every direction. The amœba if merely a drop of colloid solution would, like a drop of any jelly, gradually melt away into the surrounding water by the operation of ordinary liquid diffusion. The amœba has extensibility and retractility, and therefore cannot be an ordinary solution.

There is another point which seems to have escaped discussion by biochemists. The skin which is formed on a warm colloid solution, say of glue, is produced first because it is that part of the liquid which is cooled most quickly, being exposed to the air. The process of solidification gradually extends through the entire mass, and the extent of the film is dependent on the size of the vessel and the extension of the liquid. It is therefore indefinite. But when a new cell is formed by partition or budding a limit is set to the extension of the membrane. It continues to grow till it reaches the average dimensions of the cells which compose that particular kind of tissue. Consider the case of a vegetable cell the wall of which is composed of cellulose. One molecule after another of cellulose is generated within and is added to pre-existent molecules and cemented to them by the operation of an unknown cause, probably not ordinary chemical attraction, or what is called cohesion, because of the limit which is set to the process. The cell remains always small and microscopic, only occasionally reaching such dimensions as to become visible to the unaided eye. Ordinary chemical and physical

laws will not account for this phenomenon : no one can say as yet what it is that makes molecule stick tenaciously to molecule, forming so strong a continuous membrane, and what it is that puts a stop to the process when a sufficient extent of membrane has been produced. Neither can anyone yet say why, in a mass of cellular tissue in which cells all alike have been multiplying side by side under the same conditions, some of these cells suddenly take new forms and proceed to secrete new products, such as colouring matters, not previously found in them. If ordinary chemical and physical processes had the field to themselves, undisputed by that directive influence which is exercised by the vital principle, whatever that is, there could be no orderly arrangement in nature. Any living mass of cellular matter provided with the necessary temperature, moisture, and pabulum would develop into an indefinite mass the form of which would depend on the rate at which supplies were furnished or conditions favourable. For how can chemistry and physics explain heredity ? The seed of wheat contains within itself the incentive to produce a plant of the order of grasses, and no matter how it may be cultivated or neglected it never produces anything else.

Consider again the propagation of the animal races by the sexual process, and there can be no fear of contradiction in the statement that in the whole range of physical and chemical phenomena there is no ground for even a suggestion of an explanation. The mammalian ovum consists of a small cell about $\frac{1}{100}$ inch in diameter, while the spermatozoon is a far more minute body. The progeny which results from their interaction exhibits, more or less obviously, the characteristics of both the immediate parents or even of earlier generations. The bodily size, form, markings, and colours, as well as in the higher animals, the mental peculiarities of ancestors are reproduced. It may fairly be asked what chemical or physical property can be transmitted by any such process, or could conceivably be so stored up and utilised ?

Too much has been made of the curious observations by J. Loeb and others on the supposed fertilisation of the ova of sea urchins by immersion in solutions of sodium or magnesium salts, or by a stimulus provided by an electric current. These observations, even if not open to suspicion on account of the free diffusion of the spermatozoa of these and other creatures

in the surrounding water, prove nothing of importance in relation to the question now under discussion, which is the initiation of organic living matter from inorganic lifeless material. The ovum contains within itself the potentialities of a new generation, and the stimulus necessary to bring them into operation may well be derived from various sources in the case of creatures so low in the scale and so little removed from forms which are habitually reproduced by subdivision.

This is not the place to pursue such a discussion further. It will be sufficient to add that those who accept the purely materialistic doctrine as to the origin of life have before them the necessity of establishing a vast number of facts before such doctrine can be made generally acceptable to the scientific world. The progress which has been made in the desired direction is far from being as yet a justification for the pronouncements which have within the last few years found their way into print and which have too much the air of being uttered *ex cathedra*.

The origin of life and hence the origin of mind constitute problems which it is safe to assert will occupy mankind for generations to come. Fascinating as they are, the further we penetrate the more perplexing these problems become, and it is open to those who look at them from the standpoint of the pure physicist or the pure chemist to hold the view that physiology, being the chief handmaid of medicine, would be rendering a greater service to humanity by devoting all her great powers to furthering that branch of science rather than attempting the solution of problems which have every appearance of being insoluble. At any rate, it is urgently desirable that any statement of the new views should be communicated to the public only when the fundamental facts have been established beyond controversy, and that the biochemical and physiological student will not allow his enthusiasm to colour his hypotheses independently of the light which can be cast upon them.

The scientific chemist has a large field to himself in which will be found problems as perplexing as those which are presented to the biologist. At present who can say what is chemical affinity or attraction, what is the proper measure of valency, what is the real nature of the relation of the elements to one another? The term "energy" is freely used, and the physicist speaks commonly of potential energy and distinguishes it from kinetic energy, but he cannot define energy, he can only measure

it. "Energy," therefore, is in the same category as "life," but no one would deny its existence because he can no more say exactly what it is than he can define matter, space, or time.

The future of scientific chemistry will probably depend on the activity of research in two main directions. On the one hand, there will certainly be large additions to the long list of already known definite compounds, especially in the so-called "organic" division of compounds built up on a foundation of carbon as the characteristic element, and on the other hand, developments of physical chemistry will doubtless lead to a better knowledge of the laws which regulate chemical change and which connect together chemical constitution and physical properties. The extension of this kind of knowledge will enable the chemists of the future to calculate in advance what will be the colour and crystalline form of any compound it is proposed to make, what its physiological properties will be, and therefore its use, if any, as a medicine. Some few steps have already been taken in this direction, but there is need for a much larger body of workers properly qualified, not only by the possession of theoretical knowledge but by sufficient laboratory experience to give any results they may arrive at the indispensable quality of being trustworthy. And something further is eminently desirable, and that is some organisation of the resources which are available for the collection of facts, and for performing the large amount of routine work necessary in providing data which may be made stepping-stones to further advances. There is frequent reference to State assistance in research. This is a difficult question. While there would be practical unanimity in the feeling that State assistance should be given in the form of money there would probably be much difference of opinion as to the way in which it should be applied. State-aided or controlled institutions are apt to fall under the wheels of routine, and epoch-making discoveries are not likely to proceed from such establishments, but on this very ground they would be well fitted to carry out efficiently experimental work which has for its object the determination of physical constants and the provision of data of all kinds derived from exact observation.

The conduct of research into questions connected with special processes, materials, or patents connected with industry must be left to the manufacturers. So also must the question how far industrial research can be carried on in colleges and universities.

The association of research with the teaching of advanced chemistry is a matter which concerns the professors. And it is to be hoped that in future the governors of these institutions will see to it that there is perpetual evidence of activity in this direction, though of the results of the work done or discoveries made they may not be qualified to act as judges.

Lastly, there is the real heaven-sent researcher endowed with that kind of inspired curiosity which drives him to labour for the mere love of it, provided only that it takes the form of putting questions to nature. All that can be hoped for is that he will not be hindered by artificial obstacles created by official stupidity, and that such assistance as money can give will not be beyond his reach. For it cannot be too often repeated that *pure science*—that is, the correct observation of fact and the establishment of “law”—stands ever in practical importance before *applied science*, which is invention. But this is a hard saying, and there are still too many people who believe that the true and only business of science is to find out useful things. Even Francis Bacon, in his famous fable of the “New Atlantis,” seems to have taken this view, for in the Order or Society which he imagined under the name of “Solomon’s House” he supposes only three members of the community set apart as “Interpreters of Nature,” all the rest being occupied in drawing out of their discoveries things of use to mankind.

It is, however, only necessary to consider any application of science to useful purposes to perceive that such application became possible only at the end of a long series of observations, experiments, and arguments which occupied the labours of several generations of men. Each step forward is usually the result of some apparently trivial scrap of new knowledge acquired without regard to the question whether it is likely ever to be turned to any practical purpose.

Real progress comes from the pursuit of knowledge for its own sake.

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